CHAPTER 2
MICROCRYSTALLINE CELLULOSE AND CELLULOSE NANOMATERIAL REINFORCED POLYMER COMPOSITES – A REVIEW

Abstract

This chapter discusses the review of the earlier investigations on microcrystalline cellulose filled composites and cellulose nanomaterials reinforced composites, with special reference to PVA as matrix. Their current status has also been discussed.
2.1 INTRODUCTION

Polymer composites with enhanced properties and versatility made their ubiquitous presence in many industrial applications, including automotive, aerospace, construction, furniture, packaging etc. Fibres like aramid, carbon and glass have been extensively used as reinforcement in these composites. Eventhough, these composites are invested with favourable properties such as high strength, heat resistance and other desirable properties but they are associated with limited recyclability and above all nonbiodegradability. Therefore environmental, economic and performance issues ended in the use of natural fibres as alternative to their synthetic counterparts, without compromising performance. Not only natural fibres, but other sources like wood flour/fibres, recycled fibre-based products like newspaper, agricultural residues such as rice husks and sugarcane bagasse have also been used [1]. Since agricultural residues are rich in cellulose, they can be effectively used as reinforcement in polymer composites.

Cellulose is the most abundant natural biopolymer in the world, which is renewable and biodegradable. A number of new functional materials from cellulose have been developed for broad range of applications, due to increasing demand for environment friendly and biocompatible [2,3]. MCC, is a commercial product with over a half century of history, obtained from purified, partially depolymerised cellulose and prepared by treating cellulose with mineral acids such as 2.5 N HCl [4]. Since cellulose from different sources differ in properties like crystallinity, moisture content, surface area, porous structure, molecular mass etc., obviously MCC obtained from different sources also may vary in their properties. Moreover, physical pre-treatments can also be used significantly to modify MCC [5]. The average particle size of commercial MCC is between 50 and 350 μm.
Eventhough, wood and cotton are the principal sources to obtain MCC, a number of other source like soy bean, sugar beet pulp, bagasse, corn cob, ground nut shell, rice husks, cereal straw, Indian bamboo and luffa cylindrica etc., have also been studied as potential sources for the production of MCC [6]. Common uses of MCC include as pharmaceutical excipient, binder and texturizer, food additive, edible coatings etc. Apart from the common uses of MCC it has also been used as potential reinforcement in polymer matrix [7]. Since MCC is hydrophilic in nature, better compatibility will be obtained by hydrophilic matrices. Hydrophobic matrices can also be used by proper modification of MCC.

Physical properties of PVA depend on factors like degree of hydrolysis that is available in partially and fully hydrolysed grades, the molecular mass and water content. Partially hydrolysed PVA contains residual acetate groups with reduced crystallinity, lower melting points, easy processability, lower strength and lower water dissolution temperatures than fully hydrolysed [8]. Since PVA is water soluble, it can be processed in water medium resulting in the formation of film. Apart from being used in a number of fields, PVA has been developed for biodegradable packaging due to its biodegradability, film forming ability, flexibility, good tensile strength, as well as high oxygen and aroma barrier properties [9,10]. Since MCC is hydrophilic, the use of hydrophilic matrices like PVA enhances the compatibility, dispersion of filler, interaction between the matrix and MCC. Moreover, the composite will be environmentally benign. A number of studies dealing with the fabrication of composites of PVA reinforced with MCC, its importance and properties had appeared in the literature.
2.2 MICROCRYSTALLINE CELLULOSE (MCC) REINFORCED COMPOSITES

Blends of cellulose with PVA, prepared from mixed solutions of N,N-Dimethylacetamide-Lithium chloride by coagulation in a nonsolvent was studied by Nishiot and Manley in 1988. The results indicated that when the cellulose content increases crystallinity of PVA decreased [11].

Laka and Chernyavskaya 1996 developed thermocatalytic method for obtaining MCC (Thermocell) and studied the effect of thermocell in polystyrene. The results showed increase in density, tensile strength, bending strength than pure polystyrene [12]. The strength-deformation characteristics of low density polyethylene filled with thermocell was studied by Maskavs et al.1999. The results showed that as filler content increases, increase in elastic modulus and tensile strength was observed [13].

Hydroxypropyl cellulose (HPC), modified cellulose in different weight % was doped in PVA to produce composites. Its structural properties were studied by Zaher and Osiris in 2005. The results indicated that PVA became more thermally stable when 12 wt.% HPC were added [14]. MCC has been used as the reinforcement in PLA matrix by Mathew et al. in 2005. The composites were prepared with varying MCC contents up to 25 wt.%, wood flour (WF) and wood pulp (WP) as reference materials. The MCC-PLA composites showed lower mechanical properties than the reference materials, SEM analysis also showed poor adhesion between MCC and matrix [15].

Chakraborty et al.2006 studied the reinforcing potential of commercial MCC along with cellulose microfibers obtained from bleached softwood kraft pulp using PVA as matrix. The tensile strength of MCC-reinforced composites increased in comparison to neat PVA [16]. Chuayjuljit
et al. 2010 isolated MCC from cotton fabric waste and blended with poly (vinyl chloride). The tensile strength, Young’s modulus, moisture absorption and biodegradability of the blends were increased with increasing MCC content [17].

Composites of nylon 6 and MCC containing 2.5-30 wt.% were studied by Kiziltas et al. 2011. TG indicated that the MCC did not show significant initial degradation below 300 °C, establishing the thermal stability of composites [18]. The effect of MCC on Polypropylene (PP) and PP modified by maleic anhydride graft (PP-g-MA) and methyl acrylic acid glycidyl ester grafted PP (PP-g-GMA), using twin-screw extruder were studied by Xiuju et al. 2011. The addition of MCC led to increase in the tensile strength, impact strength, flexural strength and showed higher thermal decomposition temperatures [19].

Osiris and Manal 2012 also studied the effect of blends containing PVA and HPC. Thermal analysis showed variations in the glass transition temperature ($T_g$) indicating the miscibility of the blend systems. HPC doped PVA films was found to have improved thermal stability [20]. Hatakeyama et al. 2012 studied the effect of particle size on the properties of composites containing water absorbed polyurethane rigid foam using polyols derived from molasses and lignin [21]. Thummanukitcharoen et al. 2012 modified MCC by silane tratament (SiMCC) and prepared (SiMCC)-polypropylene composite using twin-screw extruder. TG results revealed that, during melting process the addition of SiMCC showed thermal stability enhancement of PP matrix [22].
2.3 ISOLATION OF NANOCELLULOSE

Nanotechnology is recognized as one of the fast emerging areas of technological development in the 21st century. Development of polymer nanocomposites includes multi-disciplinary areas, which can broaden the applications of polymers to many fields. Due to synergistic and hybrid properties derived from several components, they exhibit unique mechanical, electrical, optical, thermal and other properties [23]. Enhancements in properties are caused by the interaction of the polymer with nanoparticle and their good dispersion. Most of the nano fillers used, like carbon nanotubes, silica, clays, metal oxides etc., in nano composites with synthetic polymeric materials are inorganic. Their processability, biocompatibility and biodegradability are limited than those of naturally occurring organic nanomaterials [24].

Among naturally occurring, cellulose being the most abundant biopolymer gained much attention during the past few years. There are basically two categories of nano sized cellulosic particles obtained from cellulose. They are cellulose nanocrystals and microfibrillated cellulose (MFC). Mechanical treatments like cryocrushing, grinding, high-pressure homogenization, high-intensity ultrasonication, steam explosion, biological treatments like enzyme-assisted hydrolysis and chemical treatments like acid hydrolysis are often used to extract nanoobjects from lignocellulosic materials.

Cryocrushing employs the crushing of frozen pulp using liquid nitrogen, cellulose slurry is pumped at high pressure during high pressure homogenisation, grinding stones are used to breakdown the cell wall structure by shearing forces generated by the grinding stones, pre-treatment with enzyme like endoglucanase are often used before mechanical treatment [25].
High intensity ultrasonic generator is used in ultrasonic treatment [26], and treated fibres kept in autoclave under high pressures were released immediately in steam explosion process [27].

Since cellulose fibres and micro fibrils contain both crystalline and amorphous regions, on acid hydrolysis, the amorphous regions are susceptible to acid attack and under controlled conditions undergo cleavage, leaving crystalline regions intact [28]. Cellulose nanoparticles with advantages like low density, renewable nature, low energy consumption, high specific properties, modest abrasivity during processing, biodegradability, relatively reactive surface which can be used for grafting specific groups and almost unlimited availability make them suitable reinforcing filler. Since cellulose whiskers have polarity, it makes them difficult to disperse in non-polar medium. Nonpolar matrix has also been used by suitable chemical modification of the cellulose nanocrystals [28].

Beck-Candanedo et al. 2005 prepared cellulose nanocrystals from soft, hardwood, and investigated the influence of hydrolysis time and acid-to-pulp ratio. Longer hydrolysis times produced shorter, less polydisperse cellulose nanocrystals. Moreover, with increase in acid-to-pulp ratio there was reduction in the dimensions of the nanocrystals produced [29]. Bondeson et al. 2006 studied the effect of preparation conditions, concentration of sulphuric acid, hydrolysis time, temperature and the ultrasonication treatment time on cellulose nanowhiskers isolated from microcrystalline cellulose derived from Norwegian spruce (Picea abies). They observed a decrease in the length of MCC and an increase in the surface charge with prolonged hydrolysis. They also found that the optimum conditions to produce cellulose nanowhiskers was sulphuric acid of 63.5% (w/w) concentration [30]. After the optimisation of conditions by Bondeson et al. 2006, a number of sources
have been used for the isolation of nanocellulose using \( \text{H}_2\text{SO}_4 \). Wang et al. 2007 isolated the spherical cellulose nanocrystals by hydrolysis of MCC with mixed acid consisting 30% (v/v) sulphuric acid and 10% (v/v) hydrochloric acid. The degradation occurred within a narrow temperature range and shifted to higher temperature, when neutralized with NaOH solution. Cellulose with small size showed degradation at lower temperature [31]. Moran et al. 2008 extracted cellulose from sisal fibre, by means of two different procedures including acid hydrolysis, chlorination, alkaline extraction, and bleaching. The extraction procedures gave purified cellulose and nanocellulose, by subsequent acid hydrolysis. AFM of nanocellulose showed an average diameter of 30.9±12.5 nm [32]. Acid hydrolysis of native ramie fibres after chemical treatment was used to isolate aqueous suspension of elongated nanocrystals with high aspect ratio by Habibi et al. 2008. The rod-like nanocrystals obtained by TEM exhibited an average diameter 6–8 nm and a length of about 150–250 nm [33]. Wang et al. 2008 isolated spherical cellulose nanocrystals (SCNC) by acid hydrolysis of MCC using sulphuric and hydrochloric acid under ultrasonication. The authors obtained SCNC with diameters in the range of 10-180 nm, having an average diameter of 62 nm with polydispersity 49%. They observed a liquid crystalline phase under polarized optical microscope with solid contents above 3.9% [34].

Li et al. 2009 isolated cellulose whiskers from the branch-barks of mulberry (Morus alba L.), by alkali treatment followed by sulphuric acid hydrolysis. AFM image showed the diameter of whiskers are in the range 20-40 nm and length 400–500 nm [35]. Pandey et al. 2009 isolated cellulose nanowhiskers (CNW) from grass after chemical treatment followed by acid hydrolysis and mechanical treatment. The results showed that width of CNW was ~10-65 nm with a length of several nanometers [36]. Filson et al. 2009 isolated CNCs from microcrystalline wood cellulose (Avicel) and recycled
pulp obtained from wood pulp, by sono-chemical assisted hydrolysis. CNC obtained from Avicel and recycled pulp showed different morphologies. Avicel produced cellulose nanocrystals with average diameter of 21±5 nm in deionized water, while recycled pulp produced has average diameter of 23±4 nm. CNCs having length 65±19 and width 15 nm with cylindrical shape were obtained by maleic acid sono-chemical assisted hydrolysis of Avicel at 15 °C with 90% power output for 9 min [37].

Rosa et al. 2010 studied the effect of preparation conditions on thermal and morphological behaviour of cellulose nanowhiskers isolated from coconut husk fibres by sulphuric acid hydrolysis at different time. CNWs having diameters as low as 5 nm and aspect ratio of up to 60 were obtained. However, correlation between preparation conditions and particle size was not observed. Higher residual lignin content was found to increase thermal stability of the CNW [38]. Elanthikkal et al. 2010 studied the effect of temperature, reaction time, and H$_2$SO$_4$ acid concentration on cellulose microfibers isolated from banana fibre waste. As the concentration of acid increases, more stable aqueous suspensions of the cellulose product were obtained; moreover the dimensions of cellulose microfibers were reduced. XRD studies revealed that cellulose prepared by acid hydrolysis has more crystallinity than the banana fibres [39]. Teixeira et al. 2010 isolated cellulose nanofibers from white and naturally colored cotton fibres by acid hydrolysis. Suspensions of white and colored nanofibres were obtained by the acid hydrolysis of white and naturally colored cotton fibres. No significant morphological differences in shape and size were observed among them [40]. Lu and Hsieh 2010 isolated cellulose nanocrystals with rod, sphere, and network morphologies by acid hydrolysis of cotton cellulose followed by freeze-drying. Freeze drying induced mesoporosity and significantly improved specific surface than original cellulose [41].
Nanocellulose was also isolated from sugarcane bagasse (SCB) by Mandal and Chakrabarty in 2011 using acid hydrolysis. The isolated nanocellulose showed earlier onset degradation temperature compared to SCB. The results showed that the isolated nanocellulose has nano dimensions with significant conversion of cellulose I to cellulose II [42]. Teixeira et al. 2011 also isolated cellulose whiskers from SCB by alkaline peroxide pre-treatment followed by acid hydrolysis at 45°C for 30 and 75 min. The results revealed that cellulose whiskers had needle like structures with an average length of 255±55 nm and diameter of 4±2 nm, giving an aspect ratio around 64. Hydrolysis for 75 min resulted in thermally less stable whiskers, caused some damage to the cellulose crystal structure [43]. Purkait et al. 2011 isolated cellulose whiskers from sesame husk using 35% sulphuric acid. When subjected to homogenization, spherical cellulose nanoparticles (CNPs) were produced having diameters in the range of 30-120 nm [44]. Oksman et al. 2011 isolated cellulose nanowhiskers from the residue of wood ethanol industrial production. On acid hydrolysis nanowhiskers having lower thermal stability than that obtained by ultrasonication and high-pressure homogenization were produced. The AFM study showed that ultrasonication and homogenization processes resulted in whiskers having diameters 10-20 nm [45].

Johar et al. 2012 isolated cellulose fibres from rice husk by chemical treatment and cellulose nanocrystals by sulphuric acid hydrolysis of cellulose fibre. TEM analysis showed that most of the nanoparticles displayed a diameter and aspect ratio in the range of 15–20 nm and 10–15 respectively. X-ray diffraction analysis revealed that crystallinity increased with successive treatments [46]. Kenaf bast fibres were used for isolation of CNC, by Kargarzadeh et al. 2012 subjecting the fibre to alkali, bleaching and subsequent hydrolysis with sulphuric acid at different hydrolysis times. The
results showed that optimum extraction time was around 40 min at 45 °C with 65% sulphuric acid. The zeta potential measured was in the range -8.7 to -95.3 mV [47]. Bamboo cellulose nanocrystals (CNCs) were successfully prepared from the sulphuric acid hydrolysis of bamboo bleached fibres by Brito et al. in 2012. CNCs have a width of 8±3 and length of 100±28 nm [48]. Sebe et al. 2012 isolated cellulose II nanowhiskers (CNW-II) from microcrystalline cellulose with sulphuric acid, by controlling the amount of H$_2$SO$_4$ and the time of addition. The CNW-II showed average length of 153±66, height of 4.2±1.5 nm by AFM and width 6.3±1.7 nm by TEM, suggested ribbon shape morphology for whiskers [49]. Nanocrystalline cellulose (NCC) obtained from wood cellulose fibre by sulphuric acid hydrolysis was modified by grafting with glycidyltrimethylammonium chloride by Zaman et al. 2012. Due to increase in cationic surface charge density, modified NCC dispersed well in aqueous media and delayed the onset of gelation in aqueous system [50]. Lu and Hsieh 2012 isolated CNCs from rice straw by using sulphuric acid for 30 minutes (CNC30) and for 45 minutes (CNC45). Analyses showed that CNC45 was smaller than CNC30 and on freeze drying of diluted CNC suspensions both assembled into long fibrous structures. Nonporous or macroporous structures formed with CNCs by self-assembly of fibres were well aligned along the fibre axis and ultrafine fibres showed extraordinary structural stability [51].

Agro industrial residue Soy hulls were used to isolate cellulose nanocrystals by Netoa et al. 2013, using sulphuric acid for 30 and 40 minutes. The hydrolysis of 40 minutes resulted in a shorter length of nanocrystals and caused some damage on the crystal structure of the cellulose. At 30 min, the nanocrystals presented a high crystallinity of 73.5%, an average length of 122.66±39.40 nm, a diameter of 2.77±0.67 nm and an aspect ratio around 44 [52]. Peng et al. 2013 studied the effect of air-drying, freeze-drying, spray-
drying, and supercritical-drying on properties of nanofibrillated cellulose and cellulose nanocrystals (CNC). The CNCs obtained by the three methods showed similar onset temperature of thermal degradation. The crystallinity indices differ with each drying method and cellulose II content in CNCs changes as the drying method changes [53]. Jiang and Hsieh 2013 isolated CNCs and nanofibrils (CNFs) from rice straw cellulose by sulphuric acid hydrolysis, mechanical blending and by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) mediated oxidation. Sulphuric acid hydrolysis produced highly crystalline, rod-like CNCs. Mechanically defibrillated CNFs have 82.5% crystallinity. TEMPO mediated oxidation liberated the mostly uniform, finest and micrometer long, but least crystalline CNFs [54]. Morais et al. 2013 isolated nanocellulose from cotton (Gossypium hirsutum) linters using sulphuric acid of 60% (w/w). The isolated nanocrystals were 177 nm long and 12 nm wide, having an aspect ratio of 19 [55]. Fortunati et al. 2013 isolated CNC from Phormium tenax leaf fibres by acid hydrolysis. The morphological analysis carried out by field emission scanning electron microscope and tapping-mode atomic force microscopy confirmed typical needle-like structure of CNC, having acicular structure ranged from 100 to 200 nm in length and 15 nm in width [56].

Cellulose was extracted from corn/maize straw (Zea mays) by Rehman et al. 2014 using alkaline treatment and total chlorine free bleaching. Partial acid hydrolysis of cellulose with sulphuric acid at 25 °C under stirring resulted aqueous suspension of cellulose whiskers, confirmed by light scattering and TEM [57]. Low intensity ultrasonic-assisted sulphuric acid hydrolysis was used by Tang et al. 2014 to extract nanocrystalline cellulose (NCC) from MCC. NCC obtained from ultrasonic-assisted hydrolysis and conventional hydrolysis showed similar morphology having rod-like structures with width and length of 10–20 and 50–150 nm respectively. XRD
results revealed that the NCC sample from ultrasonic assisted hydrolysis contained a small amount of cellulose II [58]. Haafiz et al.2014 isolated CNW from MCC obtained from oil palm biomass by chemical swelling and acid hydrolysis methods. X-ray diffraction analysis indicated that chemical swelling improved the crystallinity of MCC and retained the cellulose I structure, but acid hydrolysis reduced the crystallinity of MCC and showed the co-existence of cellulose I and II [59]. Hu et al.2014 isolated carboxylated cellulose nanocrystals (CCN) with ammonium per sulphate and CNC with sulphuric acid from borer powder of bamboo. CCN and CNC have spherical shape with diameters of 20–50 and 20–70 nm respectively. The crystallinity of CCN and CNC were increased to 62.75 and 69.84% respectively after a series of chemical treatments [60]. Lani et al.2014 isolated nanocellulose fibre with diameters ranging from 4 to 15 nm nanocellulose from empty fruit bunch (EFB) fibre by acid hydrolysis [61].

Different sources like banana rachis, sisal, kapok, pineapple leaf and coir were used by Deepa et al.2015 for isolation of nanocellulose using combination of chemical treatments like alkaline treatment, bleaching and oxalic acid hydrolysis. The results showed that isolated nanocellulose had an average diameter in the range 10–25 nm [62]. Cellulose was isolated from tomato peels using acidified sodium chlorite and chlorine free alkaline peroxide by Jiang and Hsieh 2015. Flat spindle shaped CNCs in 15.7% yield were obtained by sulphuric acid hydrolysis of isolated cellulose. CNCs from dilute aqueous suspensions were highly crystalline cellulose Iβ fibrous mass containing mostly submicron fibres and few interconnected nanofibres. However, more uniform nanofibres assembled from CNCs were formed in 1:1 v/v tert-butanol/water mixture [63]. Onion skin was used to isolate CNC after isolating cellulose by Rhim et al.2015 using H₂SO₄ with concentrations of 45, 55, and 65%. The CNCs isolated with 45% of H₂SO₄ (CNC45) showed
the highest yield of 48.6\%, crystalinity index of 0.26 and crystallite size of 2.49 nm [64]. Van Hai et al. 2015 isolated CNCs from softwood, hardwood and non-wood plant like cotton linters, cattail and red algae by acid hydrolysis. The CNCs from cattail fibres and red algae showed higher thermal degradation temperatures and higher crystallinity indices than CNCs from wood [65]. Ghahfarrokh et al. 2015 purified beer industrial residuals (BIR) to obtain cellulose and subsequently isolated nanocellulose (NC) using acid hydrolysis/ultrasound method. The AFM analysis showed that NCs had whisker, oval and spherical shapes having average diameters between 73 and 146 nm [66].

Goh et al. 2016 studied the individualisation of MFCs from oil palm empty fruit bunches by ammonium persulphate oxidation and sulphuric acid hydrolysis. Long and network like fibrils were obtained by these methods having width 8 to 40 nm [67]. Velásquez et al. 2016, isolated nanocellulose from banana plant pseudo stems harvested at 8, 16 and 24 weeks and studied the composition, morphology and structure of cellulose during plant maturation and their influence on nanocellulose performance. Nano sized bundles obtained were polydisperse and distribution changed with maturation time. The thermal stability and allomorph ratio decreased with maturation [68]. Banana pseudo stems were also used for cellulose nanocrystal isolation by Mueller et al. using sulphuric acid. The hydrolysis time was varied to obtain maximum length of 375±100 nm and aspect ratio of 28. The surface charge density of the CNCs thus isolated was 168 mmol kg\(^{-1}\), the predominant crystal structure found was cellulose I with crystallinity of 74\% [69]. Liu et al. 2016 isolated nanocellulose from bleached corncob residue (CCR) using four different methods. Formic acid hydrolysis produced longer CNCs than by sulphuric acid hydrolysis, resulted in high crystallinity and thermal stability. TEMPO mediated oxidation resulted in CNFs with fine and
individualized structures [70]. Nanocellulose was isolated from kenaf core using electron beam irradiation followed by acid hydrolysis of the isolated cellulose by Kim et al. 2016. The results revealed that the yield of nanocellulose decreased when the absorbed dose and acid hydrolysis time increased, while the size distribution became narrow [71]. Nascimento et al. 2016 isolated nanocrystals from unripe coconut fibre by acidic hydrolysis with high acid concentration, low acid concentration, ammonium persulfate oxidation and high-power ultrasound. All the methods used converted coconut fibre into CNCs, among these high power ultrasound showed the highest efficiency in CNC isolation [72]. Mohaiyiddin et al. 2016 isolated nanocellulose from Elaeis guineensis frond (oil palm frond, OPF) through three different chemical treatments including alkaline, bleaching and acid hydrolysis processes. All results confirmed the formation of nanocellulose [73].

Since H$_2$SO$_4$ hydrolysis may introduce large number of sulphate group during hydrolysis, during pyrolysis process sulphated regions will acquire energy faster than unsulphated regions, so get eliminated quickly. Therefore, the thermal stability of nanowhisker will be comparatively less. Neutralisation with strong alkali leads to an increase in the thermal stability. Not only H$_2$SO$_4$ but other acids like HCl have been used to isolate nanocelluloses. Araki et al. isolated cellulose microcrystals from bleached softwood kraft pulp with 65% (w/w) sulphuric acid and 4 N HCl. Both treatments gave similar particle sizes and shapes. Conductometric titration of suspensions showed that the H$_2$SO$_4$ treated sample has surface charge due to the introduction of sulphate groups. But for HCl treated sample it was not noticed [74]. Chang et al. coagulated cellulose nanoparticles (CN) from NaOH/urea/water solution of microcrystalline cellulose (MC) using an ethanol/HCl aqueous solution. CNs have size about 50 to 100 nm. Compared
to MC, CN isolated has cellulose II structure [75]. Faradilla et al. isolated nanocellulose from banana pseudo-stem by TEMPO mediated oxidation combined with mild mechanical disintegration, the isolated nanocellulose has a tubular structure with diameter ranging from 7 to 35 nm [76].

**2.4 CELLULOSE NANO MATERIAL REINFORCED COMPOSITES**

The crystal modulus of cellulose was first determined in 1936 by Meyer and Lotmar and obtained a value of ~120 GPa. The value was confirmed later by experimental methods [77,78]. Sakurada et al. reported a value of 138 GPa for the crystal modulus of cellulose, which was determined using X-ray diffraction of deformed fibre bundles [77]. Many determinations were done for the crystal modulus of cellulose using X-ray diffraction, the theoretical predictions were almost in 100–160 GPa range [79–82]. Recent determination using inelastic X-ray scattering (IXS) showed a value of 220 GPa [83]. Since the elastic modulus of e-glass fibre was estimated to be 70 GPa, potential reinforcement by nanocellulose can be easily explained.

It is one of the strongest and stiffest natural nanomaterial, as an emerging nano material with important physico-chemical properties like, high tensile strength, stiffness, Young’s modulus, aspect ratio, large surface area and other intriguing electrical and optical properties. It is amenable to modifications such as sulphonation, oxidation, cationisation and grafting. Hence nanocellulose is used in diverse applications other than their use as potential reinforcement in composites.

Favier et al.1995 used cellulose whiskers, extracted from sea animal as reinforcement in composite by casting a mixture of aqueous suspensions of latex obtained by copolymerization of styrene (35% w/w) and butyl acrylate (65% w/w) and whiskers. The results showed that when whisker content was
6% (w/w), mechanical properties such as shear modulus increased by two orders of magnitude in the rubbery state of the polymeric matrix [84]. Since then large number of polymers were used as matrices for the preparation of nanocomposites. Helbert et al. 1996 incorporated cellulose microcrystals from wheat straw in poly (styrene-co-butyl acrylate) latex. The whiskers bring reinforcing effect at temperatures higher than the glass transition temperature ($T_g$) of the matrix and improved the thermal stability of the composite [85]. Chazeau et al. 1998 studied nanocomposites with plasticized poly (vinyl chloride) as matrix and cellulose whiskers from tunicate as reinforcement [86]. Angles and Dufresne 2000 studied nanocomposite from glycerol plasticized waxy maize starch as the matrix and a suspension of tunicin cellulosic whiskers as reinforcement [87]. Maren and William 2002 prepared nanocomposite using cellulose acetatebutyrate as matrix and modified nanocrystals from bacterial cellulose microfibrils as reinforcement. The unmodified cellulose crystals showed better reinforcement characteristics compared to modified crystals [88]. Samir et al. 2004 studied nanocomposite using poly (oxyethylene) as the matrix and stable aqueous suspension of cellulose nanocrystals from tunicate as the reinforcing phase [89].

By using hydrophilic matrix better interaction between matrix and filler takes place leading to improvement in properties. Zimmermann et al. 2004 studied the effect of dispersed cellulose fibrils or fibril bundles from sulphite pulp as reinforcement in PVA. The films showed increases in modulus of elasticity and tensile strength than PVA [90]. Hydrophobic matrix like polypropylene was also studied by Ljungberg et al. 2005 using three types of cellulose whiskers, with various surface and dispersion characteristics [91].
Bhatnagar and Sain 2005 studied the effect of nanofibers from flax bast fibers, hemp fibers, kraft pulp, and rutabaga in PVA. The tensile strength of nanocomposites developed from rutabaga containing 90% PVA and 10% nanofiber showed an increase from 69 to 118 MPa. The different nanocomposites showed four to five fold increase in Young’s modulus [92]. Bruce et al.2005 made nanocomposites with PVA using purified cell wall fragments (PCWF) and fibrillised cell wall material (FCWM). The results showed that strength of composite at a volume fraction of 50% fibre content obtained from FCWM, increased by five times than PVA and composite stiffness also increased [93].

Wang et al.2006 studied nanocomposites using soy protein isolate plastics as matrix and whisker from cotton linter pulp as reinforcement. The results showed that strong interactions occurred with the addition of cellulose whisker [94]. Chakraborty et al. studied the reinforcing potential of cellulose microfibers obtained from bleached softwood kraft pulp in PVA. The mechanical strength measurements showed increased tensile strength by two fold and a 2.5 fold increase in stiffness with 5% microfibre loading. Decrease in strength and stiffness at higher loading was another observation [95].

Wang and Sain 2007 dispersed nanofibres from soy bean stock by chemo-mechanical treatments in PVA, up to 10% nano fiber content (SBN). The tensile strength of 5% nanofibre blend PVA film increased by five-fold [96]. The same authors also studied the reinforcing ability of nanofibre from soy bean source in three different polymers PVA, PP and PE. The tensile strength increased by fivefold at 5 wt.% fibre content for PVA composites. The DMA showed the addition of SBN improved the thermal properties of PVA and influenced the tanδ peak and storage modulus [97]. Leitner et al. 2007 studied reinforcement of nanofibrils from sugar beet chips using PVA
and phenol-formaldehyde as matrices. The best mechanical performance was achieved with phenol-formaldehyde resin having nanofibril content of 10% [98]. Petersson et al. 2007 studied nanocomposites of PLA and CNW obtained from MCC [99]. Cao et al. 2007 prepared nanocomposite films containing suspension of cellulose nanocrystals from flax fibre as filler and polycaprolactone based waterborne polyurethane (WPU) as the matrix. The films showed a significant increase in Young’s modulus and tensile strength [100].

Li et al. isolated cellulose whiskers from cotton linter and used as reinforcement in chitosan. With increasing whisker content from 0 to 15–20 wt.%, the tensile strength increased, displayed excellent thermal stability and water resistance [101]. Lu et al. 2008 studied the properties of PVA films reinforced with 1, 5, 10, and 15 wt.% of MFC obtained from kraft pulp. The results showed that $T_g$ and $T_m$ are independent on the MFC content. DMA results showed increase in the storage tensile modulus in the glassy state when the MFC content increased. Young’s modulus and tensile strength of the composite increased for composites containing MFC up to 10 wt.% [102]. Paralikar et al. 2008 studied PVA barrier membrane containing cellulose nanocrystals (CNXLs) isolated from Whatman 1 filter paper with poly (acrylic acid) (PAA) as a crosslinking agent. The membrane having 10% CNXLs/10% PAA/80% PVA exhibited the highest tensile strength, tensile modulus and toughness. Differential thermogravimetric studies also supported the tensile test results. Moreover, initial degradation temperatures of composites with modified CNXL by carboxylation and unmodified CNXL increased. But composites with modified CNXL showed higher initial degradation temperature [103]. Roohani et al. 2008 isolated cellulose whiskers from cotton linter and used as filler in PVA having different molecular weights and degrees of hydrolysis. The results showed increased
reinforcing effect when the degree of hydrolysis of the matrix increases. This leads to an increase of the glass temperature, decrease of both the melting point and degree of crystallinity of the polymeric matrix in dry atmosphere. Whisker addition increases $T_g$ regardless the degree of hydrolysis for moist samples. Reinforcing effect was further confirmed by DMA and tensile tests \[104\].

Lee \textit{et al.} 2009 studied the effect of acid treatment and filler concentration of nanocellulose obtained by acid hydrolysis of MCC with different concentrations of hydrobromic acid (HBr) in PVA. The tensile strength of films with 1.5 M HBr hydrolysis showed the value 73 MPa at the loading of 1 wt.%, 49.0% higher than neat PVA film and the value decreased at higher loading. The composite film containing nanocellulose hydrolysed with 2.5 M HBr showed 8.2, 11.6 and 27.7% higher tensile strength at loading levels 1, 3, and 5 wt.% respectively than those treated with 1.5 M HBr. The thermal properties of PVA composite films were significantly improved with the increase in the nanocellulose loading \[105\]. Qua \textit{et al.} 2009 characterised nanocomposite of PVA reinforced with nanofiber from MCC and flax fibre using ball milling, acid hydrolysis, and ultrasound. The films showed enhanced thermal and mechanical properties with small addition of cellulose nanofibres. DMA results showed that the use of cellulose nanofibers obtained by acid hydrolysis leads to outstanding and unusual mechanical properties \[106\]. Cheng \textit{et al.} 2009 studied the effect of cellulose fibrils in micro and nanoscales generated through high intensity ultrasonication from regenerated cellulose fiber (RCF), pure cellulose fiber (PCF) and MCC as reinforcement in PVA. Most of the small fibers improved the mechanical properties of PVA significantly \[107\].
Souza et al. 2010 isolated nanofibers from curaua fibres and studied their effect in PVA. The results indicated that with 4% of fibre loading, the stress and modulus of the composite increased by 36% and 67%, respectively and with 5% of fibre loading Young’s modulus again increased [108]. Peresin et al. 2010 prepared composite mats containing cellulose nanocrystals (CN) through electro spinning of PVA having different acetyl concentration. Cellulose nanocrystals induced 3 fold increase in the storage modulus of fully hydrolysed PVA, while this was not observed in partially hydrolysed PVA [109]. Ibrahim et al. 2010 isolated spherical nano cellulose from cotton linter, linen and used as reinforcement in PVA. Composite film containing 20% of nano cellulose particles from linen increased the mechanical properties, while 40% and 60% resulted in decrease in the tensile strength [10]

Kamphunthong et al. isolated nanofibres from para rubberwood and used as reinforcing filler in PVA. The composites gave enhancement in modulus by 100% and strength by 80%, with the addition of 7 wt.% fibre. DMA and DSC also revealed the strong interaction between the fibres and PVA [110]. Zhang et al. 2011 studied the mechanochemical activation of cellulose by pan milling on cellulose-PVA composites using melt mixing, containing formamide and water as plasticizer. The tensile strength of cellulose-PVA composites increased from 8.8 to 16.4 MPa when pan milling cycles of cellulose increased, while elongation at break increased from 76.8 to 374%. The composites exhibited enhanced thermal stability [111]. Frone et al. 2011 prepared cellulose nanofibre reinforced PVA composites by the action of hydrodynamic force along with ultrasound. Difference in size of nanofibre was observed using different ultrasound condition, with no change in the crystalline structure of nanofibre. The tensile strength and modulus of the PVA increased significantly by the addition of nanofibre and composite showed slightly higher onset degradation temperature [112]. Bulota et al. 2011 prepared PVA composites film reinforced with mechanically microfibrillated (MFC) birch pulp. Increase in Young’s modulus and tensile
strength were observed for MFC below 10% (w/w) content, by providing degassing. Higher strength and stiffness were showed by composites conditioned at 45% relative humidity (RH) than at 55% RH [113]. Cho and Park 2011 isolated nanocellulose (NC) from commercial MCC and added as reinforcement in different weight % in PVA. As the NC content increases the tensile modulus and strength of the nanocomposite improved, but decreased at the higher NC content of 7 wt.% [114]. Uddin et al. 2011 prepared nanocomposite of PVA reinforced with highly oriented colloidal suspension cellulose whiskers (CWs) obtained by acid hydrolysis of commercial cotton cellulose powder in PVA. Spun fibre containing 5 wt.% CW showed higher drawability than neat PVA fibre, leading to orientation of CWs in the matrix. The 5% CW-PVA fibre has the highest tensile strength of 1.89 GPa compared to the 1.47 GPa of neat PVA fiber [115].

Kaboorani et al. in 2012 studied the effect of nanocrystalline cellulose (NCC) in poly (vinyl acetate) (PVAc) as a wood adhesive. The results showed that NCC can improve bonding strength, hardness, modulus of elasticity and creep of PVAc film. Thermal stability of PVAc improved significantly [116]. Martínez-Sanz et al. prepared ethylene-vinyl alcohol copolymer (EVA) nanocomposite, by melt compounding plant cellulose nanowisker (CNW) and bacterial cellulose nanowiskers (BCNW). The results showed that BCNW up to 4 wt.% can be introduced without causing significant agglomeration, but increasing the CNW concentration up to 3 wt.% induced agglomeration. DSC result revealed that poor dispersion leads to significant reduction in crystalline content [117]. Qiu and Netravali 2012 prepared PVA composites reinforced with MFC containing glyoxal as the cross linking agent. The MFC–PVA composites showed good tensile properties and thermal stabilities, get further increased by crosslinking [118]. Sharma et al. 2012 isolated NFC from processed ryegrass and used as reinforcement in PVA. NFC-PVA composites with NFC content of 5 wt.%, exhibited enhanced Young’s modulus and thermal stability by factors of 2.5
and 2 respectively than control [119]. Li et al. 2012 isolated nanocrystalline cellulose (NCC) from MCC by high-intensity ultrasonication and used as reinforcement in PVA. The modulus of PVA with 8 wt.% NCC was found to be 2.4 times larger than that of pure PVA [120].

Liu et al. 2013 defibrillated paper pulp into cellulose nanofiber (CNF) by mechanical grinding and high pressure homogenization, used as reinforcement in PVA to prepare transparent composite films. The addition of CNF improved the crystallinity, mechanical strength, Young’s modulus, T_g and thermal stability of the PVA [121]. Li et al. 2013 prepared nanocomposite film of PVA containing nanocellulose fibrils (NCF) from bleached hard kraft pulp through high-intensity ultrasonication. The results showed that at 4 wt.% of NCF content, tensile strength and Young’s modulus of the PVA composites increased to 1.86 and 1.63 times than neat PVA and composites has excellent transparency [122]. Alves et al. 2013 isolated CNC from corncob by sulphuric acid hydrolysis at 45 °C for 30, 60 and 90 min, and studied their reinforcing capability with PVA. The CNC-PVA composites having reinforcement of nanocellulose with 60 minute hydrolysis duration (CNC60) has showed an increase in tensile strength of 140.2%, when 9 wt.% of CNC60 was incorporated [123]. Bio-nanocomposite reinforced with CNC extracted from commercial MCC (CNC-MCC) and from two types of natural fibres, phormium tenax and flax (CNC-Flax) was prepared by Fortunati et al. 2013. The addition of CNC resulted in increased tensile strength for CNC-MCC and CNC-Flax compared to the PVA matrix [124].

Virtanen et al. 2014 used chemically modified NFC by allylation and epoxidation as reinforcement in a PVA matrix. Enhancement in modulus and strength of the pure PVA film by 474% and 224% respectively was observed by the addition of 1 wt.% epoxy-NFC, film showed transmittance of 83% and improved the crystallinity of PVA. The results indicates the significant effect of chemical modification of NFC on mechanical properties of PVA [125].
Peng et al. 2014 studied the effect of short cellulose nanofibrils (SCNF) isolated mechanically from hard wood pulp after enzymatic pre-treatment in PVA. The result revealed that when small amounts of SCNF were added, PVA crystal orientation increased and decreased as the SCNF content increased above 2 or 3%. The SCNF-PVA composite fibre with 6% SCNF showed ultimate strength and modulus 60 and 220% higher than that of neat PVA [126]. Li et al. 2014 isolated NCFs from chemical-thermomechanical pulps (CTMP) using ultrasonication and used as reinforcement in PVA. Composites having NCF content of 6 wt.% showed better properties. The tensile strength, Young’s modulus and thermal stability of composites improved significantly [127]. Zhang et al. 2014 studied the effect of isolated CNC from MCC and compounded with PVA through melt processing along with water and formamide as plasticizer, by injection moulding. Improvement in tensile strength from 32 to 58 MPa and modulus from 175 to 1,252 MPa by the addition of 7 wt.% CNCs were observed. The presence of CNCs reduced the volume shrinkage of PVA nanocomposite on drying and their water leaching rate [128].

Kakroodi et al. 2015 studied the effect of CNF from the skin of the beavertail cactus (Opuntia Basilaris) isolated by chemo-mechanical technique in PVA. The modulus and strength of the PVA matrix increased significantly by the addition of nanofibre, while the elongation at break decreased. TG showed that the inclusion of nanofibres resulted in increase in the thermal stability of composites [129]. Voronova et al. 2015 studied the thermal stability of PVA nanocomposite using CNC from commercial MCC as reinforcement. Thermal stability of the composites improved with CNCs content of 8–12 wt.%, but decreased when more than 12 wt.% CNCs content was used [130].
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