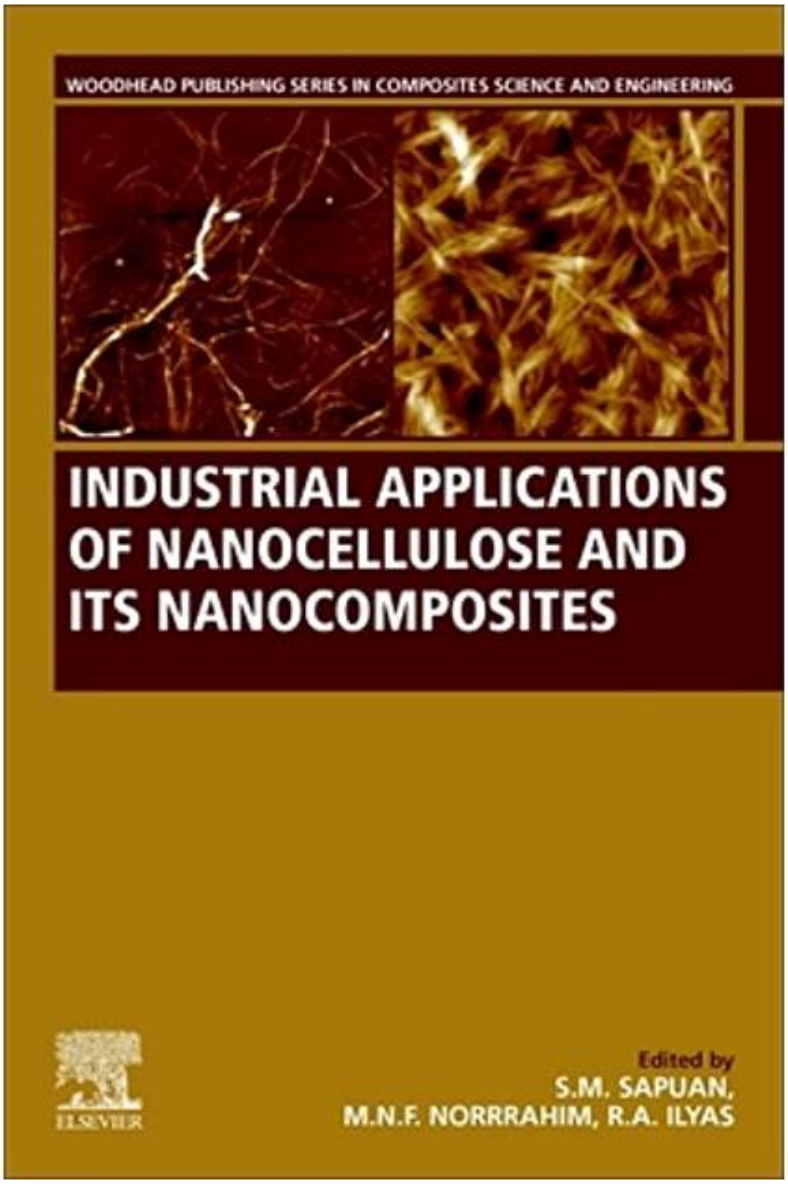

Industrial Applications of Nanocellulose and Its Nanocomposites

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Preface

Industrial Applications of Nanocellulose and Its Nanocomposites provides an extensive, up-to-date overview of this fast-moving area of study from the perspectives of prominent researchers in academic, industrial, and government or private research laboratories. This is an exciting time to be in as, moving beyond scientific curiosity, nanocellulose is starting to hit the marketplace. Nanocellulose is a versatile material that is receiving a lot of attention from scientists in several fields such as automotives, composites, adsorbents, paints, coatings, medical implants, electronics, cosmetics, pulp and paper, tissue engineering, packaging, and aerogels. Current trends show that research related to recent developments of nanocellulose is increasing and covers several aspects including synthesis, surface modification, and improvement of the properties of nanocellulose, bearing in mind the targeted applications.

The objectives of this book are to reflect on recent advancements in the design and fabrication of nanocellulose and to discuss the important requirements for each application, along with the challenges that might arise. This book also includes an overview of the current economic perspectives and safety issues related to nanocellulose. The potential of nanotechnology and nanocomposites in various sectors of research and applications is promising and attracting increasing investment. For this reason, this book will benefit end users such as students, researchers, and industry players. Each chapter explains in detail the important role of nanocellulose, including the advantages and limitations of its specific applications. The book includes commentary from leading industrial and academic experts in the field who present cutting-edge research on advanced materials based on nanocellulose. Improvement features and recommendations are also provided to pave the way to new horizons for nanocellulose, and its applications. Therefore, this book will offer guidance to current, new, and future researchers in nanocellulose to strategize their work to meet the current demands. In terms of commercialization, this book will steer industry players to identify the potential uses of nanocellulose in their products. These same concepts are available elsewhere in the preface. Finally, thoughts on the future directions of nanocellulose-based materials have been included in some chapters.

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Enhanced thermal stability of cellulose nanocrystals for processing polymer nanocomposites at a high temperature

13

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Chapter outline

13.1 Introduction

CNC has emerged as an attractive filler for polymer composites due to its intrinsic mechanical properties. Low loading of CNC between 0.5 and 1 wt% in the polymer matrix has demonstrated an extraordinary increase in tensile strength of various polymer composites for instance 20% and 35% of improvement in polyvinyl(acetate) (Nozaki & Lona, 2021)and polylactide (Chai et al., 2020) respectively. However, the process to fabricate CNC/polymer nanocomposites often involved conventional method which is not suitable for scalable production. A conventional method like solvent casting constitutes a problem in terms of production speed and environmental issues due to the high solvent usage (Jyoti, Basu, Singh, & Dhakate, 2015). Thus, the melt compounding method consists of extrusion and molding is preferred to suit industrial-scale production and demand. Melt compounding which is commonly employed by thermoplastic polymer operating at high processing temperature from as low as 120°C for common polyethylene (Zaaba & Ismail, 2019) up to 390°C for polymer-like Polyether ketone (Das et al., 2020). Table 13.1 offers an overview of techniques that were used recently to produce CNC-based composites with some respected examples.

One challenge in utilizing CNC in polymer composites specifically thermoplastic polymer fabricated through melt compounding method is that their thermal stability

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Table 13.1 Techniques and fraction of CNC applied in CNC/polymer nanocomposites.

Technique	Polymer matrix	Fraction of CNC (wt%)	Ref.
Extrusion and/or molding	Polyethylene	1.5	Inai, Lewandowska, Ghita, and Eichhorn (2018)
	Polyethylene	1.0	Gray, Hamzeh, Kaboorani, and Abdulkhani (2018)
	Polypropylene	2.0	Sojoudiasli, Heuzey, and Carreau (2018)
	Polystyrene	10	Nagalakshmaiah, Nechyporchuk, El Kissi, and Dufresne (2017)
	Polyester	1–3	Zheng, Clemons, and Pilla (2019)
Solvent casting	Poly (lactic acid)	1.0	Hao et al. (2018)
	Waterborne Polyurethane	5	Mondragon et al. (2017)
	Poly (vinyl alcohol)	10	Popescu (2017)
	Acrylonitrile Butadiene Styrene	1	Ma, Zhang, and Wamg (2017)
	Rubber latex	1	Jailudin and Mohd Amin (2020)

which is close to melting temperature most of the polymer. This tends to rise degradation and discoloration of the extruded nanocomposites (Abhijit, Johannes, Sahlin-Sjövold, Mikael, & Boldizar, 2020). Thus, recent researches are actively producing CNC with enhanced thermal stability to counter this problem.

13.2 Process to enhance the thermal stability of CNC

The most common isolation method to produce CNC is by using the sulphuric acid hydrolysis method. This method is preferable by most researchers due to its simple process flow, established protocols, and high production yield (2015). However, CNC produced has low thermal stability resulted by substitution of sulfate functional group over hydroxyl group which may be promoting dehydration reactions and act as flame retardants to the CNC. The onset degradation temperature mostly recorded values around 210–240°C (Zhang et al., 2020). Table 13.2 shows the onset degradation temperature of CNC according to the acid employed for the hydrolysis process.

Recently, ionic liquid (IL) also has been used to improve the thermal stability of CNC. IL is a green solvent with negligible vapor pressure which has multiple functions and initially is used in polymer modification. The attempt of ionic liquid-like 1-allyl-3-methylimidazolium chloride as a plasticizer has surprisingly improved the thermal stability of CNC (Liu, Guo, Nan, Duan, & Zhang, 2017). The results were obtained due to the ability of IL to partial desulfurization of CNC and the thermal degradation recorded at 240°C. Following that, a simple method of mixing IL with CNC was performed by rotary evaporate procedure, and it is able to increase the thermal

Table 13.2 Onset degradation temperature of CNC produced through acid hydrolysis.

Type of acid	Onset degradation temperature (°C)	Ref.
Sulphuric acid	200–240	Bano and Negi (2017), Xing, Zhang, Tu, and Hu (2018), and Zhang et al. (2020)
Hydrochloric acid	244	Hastuti, Kanomata, and Kitaoka (2018)
Phosphoric acid	260–310	(Espinosa, Kuhnt, Foster, & Weder, 2013), (Frost & Foster, 2020), Zhang et al. (2020), and (Wang et al., 2019)
Formic acid	300–325	Lv et al. (2019) and Du et al. (2017)
Mixed acids	250–300	Cheng et al. (2020), Vanderfleet et al. (2019), Wang, Yao, Zhou, and Zhang (2017), and Yu, Qin, Sun, Yan, and Yao (2014)

stability up to 210°C and increase the miscibility with polymer matrix as well (Song et al., 2018). Other than that, research also has shown that doing post alkali treatment on CNC film also has successfully erased the sulphate group resulting in a remarkable enhancement in thermal properties (Nan et al., 2017). This method successfully achieves thermal degradation at 260°C.

Alternatively, phosphoric acid or mixed acids (combination of two or more acids in hydrolysis process) have been utilized to isolate CNC with better thermal stability. Phosphoric acid, formic acid, and mixed acid are able to increase the thermal stability up to 300°C which is excellent to be reinforced with high-performance thermoplastic polymer with a processing temperature of more than 200°C (Das et al., 2020).

Other than that, mechanical methods like ultrasonication, homogenizer, and milling are also gaining high attention to be used in producing CNC. These methods are used as a posttreatment to produce CNC. CNC produce through this method provides good thermal stability as shown in Table 13.3 in fact it has a high production yield which is suitable for high scale production. In addition, this method also consumes low preparation time, acid/solvent usage, and energy (Mohd Amin, Annamalai, & Martin, 2017).

Overall, the degradation temperature of CNC able to be improved up to 300°C which falls in the temperature range of most high-performance thermoplastic polymer processing using the melt compounding method. This significant increase in thermal stability will boost up the employment of CNC as a reinforcing filler for polymer composite.

Table 13.3 Onset degradation temperature of CNC produced through a mechanical method.

Type of acid	Onset degradation temperature (°C)	Ref.
Ball milling	258–263	Mohd Amin, Annamalai, and Martin (2017)
Ultrasonication	250	Mohd Amin, Annamalai, Morrow, and Martin (2015)

13.3 Thermally stable CNC-reinforced polymer nanocomposites

Here the discussion on the CNC/polymer nanocomposite processed through melt compounding method is reviewed. The works are done to avoid thermal degradation of CNC either using preprocess to the CNC (grafting, modification, etc) or using ready thermally stable CNC to be reinforced with polymer and further process with melt compounding method with the purpose of high scalability production to suit the industry demand.

The first part will discuss the nanocomposites work which are using preprocess method to the low thermal stability of CNC. Polylactic acid (PLA) is one of the most promising biopolymers with exceptional properties, is being used in a wide variety of applications in diverse fields (Mao, Tang, Zhao, Zhou, & Wang, 2019). Research by Dhar, Tarafder, Kumar, and Katiyar (2016), has successfully fabricated CNC/PLA nanocomposite by using reactive extrusion. In this work, the CNC has been grafted with PLA using dicumyl peroxide as a crosslinking agent. Significantly, the grafted PLA chains shield the sulfate and hydroxyl groups of CNCs, thereby enhancing the compatibilization with the PLA matrix and preventing thermal degradation during extrusion. The extrusion processing temperature was at 180°C and the extrudate did not show any degradation or discoloration as shown in Fig. 13.1 with coding "PLAD CNC1".With 1 wt% of CNC in the PLA matrix, the tensile strength of the CNC/PLA nanocomposite recorded 40% of improvement from neat PLA. A similar biopolymer which is PHBV (poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)), a family of bacterially-derived linear polyesters adopted a similar method (Zheng et al., 2019) as well. The maximum extrusion processing temperature is 160°C.

Next is polyamide which has garnered a lot of interest for its potential use in various applications ranging from deep-sea oil production to lightweight replacements for metals and rubbers in automobiles and aircrafts, to high-performance athletic shoes (Oliver-Ortega et al., 2019; Thokala, Kealey, Kennedy, Brady, & Farrell, 2017).

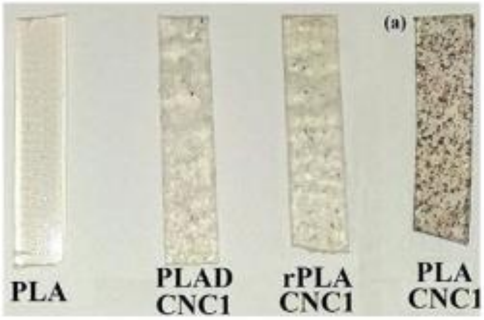

Fig. 13.1 Pictorial comparisons of the neat PLA, PLADCNC1 and rPLACNC1strips with PLA/CNC 1 wt% extruded by simple melt blending.
Reproduction of image from Dhar, P., Tarafder, D., Kumar, A., & Katiyar, V. (2016). Thermally recyclable polylactic acid/cellulose nanocrystal films through reactive extrusion process. *Polymer, 87*, 268–282. https://doi.org/10.1016/j.polymer.2016.02.004 with permission from Elsevier.

Polyamide (PA) 12 has been reinforced with thermal stable CNC produced through phosphoric acid hydrolysis and was managed to be processed through melt compounding method (Nicharat, Sapkota, Weder, & Foster, 2015). 1–20 wt% of CNC in the PA matrix was extruded at a temperature of 190°C and the tensile strength was increased from 40 to 72 MPa. Meanwhile a work with another type of PA which is PA 11 also able to process using melt compounding method as well by using preprocessing/premixing methods which is planetary ball milling and melt-compounding (rollerblade mixing) without the addition of processing aids or additional surface functionalization of CNC (Venkatraman, Gohn, Rhoades, & Foster, 2019). CNC used is from the acid hydrolysis process was further milled with PA 11. This process uses ball-bearing collisions to mechanically weld together two materials in the solid-state without solvents. Then, the PA12/CNC was melt compounded at temperature 190°C. The film fabricated as shown in Fig. 13.2, the method used able to prevent degradation of CNC as the film was compared with the sample without milling and just directly mixed and compound the PA11 and CNC. The tensile strength of the PA11/CNC with the milling process.

Another example of thermoplastic used with CNC is polypropylene (PP). PP can be fabricated to fiber and fabrics, film, injection, and blow molding products as well

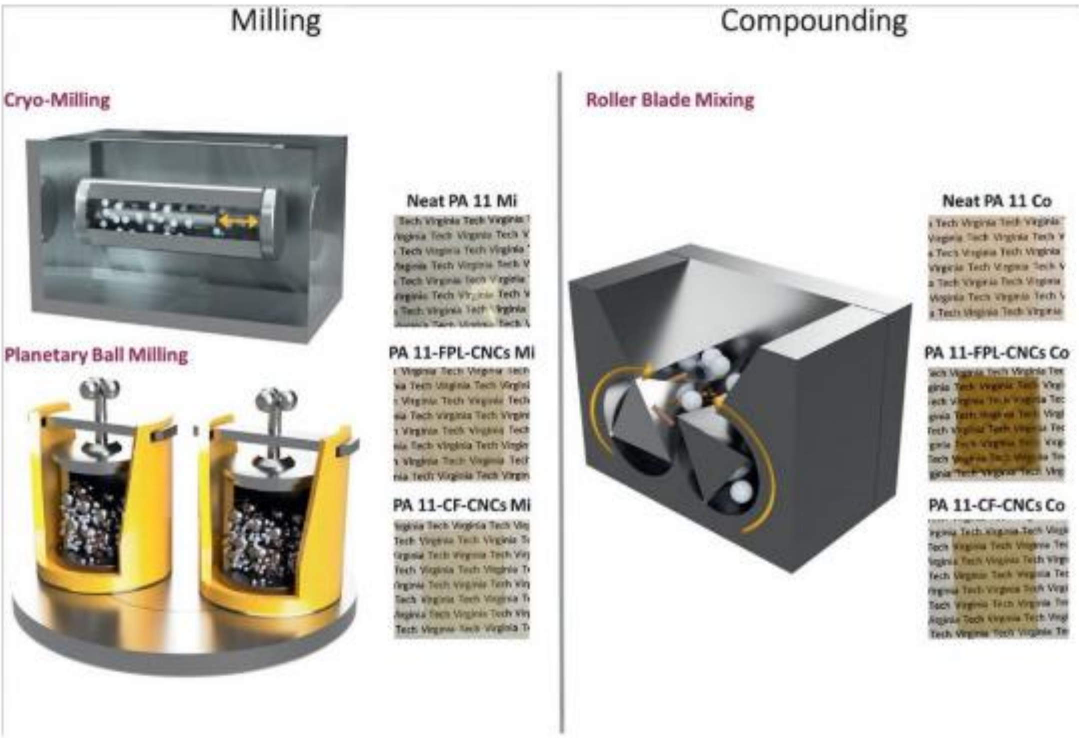

Fig. 13.2 PA11 and PA11/CNC nanocomposite film fabricated via melt compounding with preprocess with milling (left) and without milling (right).
Reproduction of image from Venkatraman, P., Gohn, A. M., Rhoades, A. M., & Foster, E. J. (2019). Developing high performance PA 11/cellulose nanocomposites for industrial-scale melt processing. *Composites Part B: Engineering, 174*, 106988. https://doi.org/10.1016/j.compositesb.2019.106988 with permission from Elsevier.

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