Micro- and Nanostructured **POLYMER SYSTEMS**

From Synthesis to Applications



Editors Sabu Thomas, PhD, Robert A. Shanks, PhD, Jithin Joy





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LIST OF ABBREVIATIONS

AA	acrylic acid
AFM	atomic force microscope
AgNPs	silver nanoparticles
APS	ammonium per sulfate
BC	bacterial cellulose
BCNC	bacterial cellulose nanocrystals
BER	bulk electrical resistivity
BFE	basalt fabric reinforced epoxy
BFP	basalt fabric reinforced polyester composite
BM	batch mixer
BNN-PS	barium sodium niobate-polystyrene
CF	carbon fibers
CNCs	cellulose nanocrystals
CNFs	carbon nanofibers
CNTs	carbon nanotubes
COD	chemical oxygen demand
CP/MASNMR	crossed polarization and magic angle spinning nuclear magnetic
	resonance
CPE	chlorinated polyethylene
СТ	computer tomography
CVD	chemical vapor deposition
DIDP	di-isodecyl phthalate
DMM	digital multi-meter
DSC	differential scanning calorimeter
DSM	twin-screw micro-compounder
EAPaP	"smart material" or "electroactive paper"
EM SE	electromagnetic shielding effectiveness
EMC	electromagnetic compatibility
EMI	electromagnetic interference
ENR	epoxidized natural rubber
ESD	electrostatic discharge
ESD	electrostatic dissipation
ETFE	ethylene tetrafluoroethylene
FTIR	fourier transform infrared
FWHM	full width at half maximum
GC	gas chromatography

Gd ₂ O ₃	gadolinium (III) oxide
GPC	gel permeation chromatography
HALS	hindered amine light stabilizer
HR-TEM	high resolution transmission electron Microscopy
HPLC	high performance liquid chromatography
HPMC	hydroxypropyl methylcellulose
HT	thermal treatment
IDT	initial decomposition temperature
i-PMMA	PMMA isotactic
IPN	inter penetrating network
KGM	starch-konjac glucomannan
КОН	potassium hydroxide
LLDPE	linear, low-density polyethylene
LSPR	localized surface plasmon resonance
MA	maleic acid
MB	methylene blue
MBTS	mercaptobenzothiazyl disulfide
mCPBA	<i>m</i> -chloroperoxybenzoic acid
MEKP	methyl ethyl ketone peroxide
MFA	multifunctional acrylates
MWNT	multi-walled carbon nanotubes
MWS	Maxwell-Wagner-Sillars polarization
nano-CaCO ₃	nanoscale calcium carbonate
NBR	acrylonitrile-butadiene rubber
NMBA	N,N'-methylenebisacrylamide
NRF	National Research Foundation
OM	optical microscopy
PAAAM	poly(acrylate- acrylic acid-co maleic acid)
PAM	polyacrylamide
PAMA	poly(n-amyl methacrylate)
PBA	poly(butyl acrylate)
PBMA	poly(butyl methacrylate)
PCP	polychloroprene
PDMDPS	polydimethyldiphenylsiloxane
PDPS	polydiphenylsiloxane
PE	polyethylene
PEA	poly(ethyl acrylate)
PEG	polyethylene glycol
PEMA	poly(ethyl methacrylate)
PEO	polyethylene oxide
РНО	poly(β-hydrox-yoctanoate)
PIB	poly(iso butylene)

List of Abbreviations

PLA	polylactic acid
PMMA	poly(methyl methacrylate)
POE	polyolefin elastomer
POM	polyoxymethylene
PPy	polypyrrole
PVA	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
PVP	poly (vinyl pyrrolidone)
RGA	residual gas analyzer
SAP	superabsorbent polymers
SAXS	small-angle x-ray scattering
SCE	saturated calomel electrode
SEI	secondary electron image
SEM	scanning electron micrographs
SEM-EDX	scanning electron microscopy-energy dispersive X-ray
SERS	surface enhancing Raman scattering
SICART	sophisticated instrument center for applied research and testing
SMA	styrene maleic anhydride
SP/s	seaweed polysaccharide/s
SPHs	SUPERPOROUS hydrogels
s-PMMA	syndiotactic
TEM	transmission electron microscopy
TG	thermogravimetry
TGA	thermo gravimetric analyzer
TMTD	tetramethylthiuram disulfide
ToF-SIMS	time of flight secondary ion mass spectrometry
TPS	thermoplastic starch
TPU	thermoplastic polyurethane
UHV	ultra-high vacuum
UPVC	unplasticized poly(vinyl chloride)
USEPA	US Environmental Protection Agency
UV/Vis	UV/visible spectroscopy
WHO	World Health Organization
WVTR	water vapor transmission rate
XRD	X-ray diffraction
X-RD	X-ray diffractometry

PREFACE

This book, **Micro- and Nanostructured Polymer Systems: From Synthesis to Applications**, describes the recent advances in the development and characterization of multicomponent polymer blends and composites. It covers occurrence, synthesis, isolation and production, properties and applications, modification, and also the relevant analysis techniques to reveal the structures and properties of polymer systems. Bio-based polymer blends and composites occupy a unique position in the dynamic world of new biomaterials. Natural polymers have attained their cuttingedge technology through various platforms; yet, there is a lot of novel information about them, that is discussed in this book.

This book covers topics such as biopolymer-synthetic systems, nanomaterialpolymer structures, multi-characterization techniques, polymer blends, composites, polymer gels, polyelectrolytes and many other interesting aspects. It is written in a systematic and comprehensive manner. The content of the present book is unique. It covers an up-to-date record on the major findings and observations in the field of micro- and nanostructured polymer systems.

This book will be a very valuable reference source for university and college faculties, professionals, post-doctoral research fellows, senior graduate students, polymer technologists, and researchers from R&D laboratories working in the area of nanoscience, nanotechnology, and polymer technology.

Finally, the editors would like to express their sincere gratitude to all the contributors of this book, who extended excellent support to the successful completion of this venture. We are grateful to them for the commitment and the sincerity they have shown toward their contribution in the book. Without their enthusiasm and support, the compilation of this volume could not have been possible. We would like to thank all the reviewers who have taken their valuable time to make critical comments on each chapter. We also thank the publisher Apple Academic Press for recognizing the demand for such a book and for realizing the increasing importance of the area of micro- and nanostructured polymer systems and for starting such a new project.

-Sabu Thomas, Robert A. Shanks, and Jithin Joy

NATURAL POLYMER BLENDS AND THEIR COMPOSITES: MICRO AND NANO STRUCTURED POLYMER SYSTEMS

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ABSTRACT

There is a global interest in replacing synthetic polymer composites for daily applications with environmentally friendly alternatives from renewable resources. The large quantities of the petroleum-based polymeric materials raised a negative effect on the environment. Nanotechnology has a great potential in the development of high-quality biopolymer-based products. Biopolymers are attracting considerable attention as a potential replacement for petroleum-based plastics due to an increased consciousness for sustainable development and high price of crude oil. Biopolymers ideally maintain the carbon dioxide balance after their degradation or incineration. By using biodegradable grades, they will also save energy on waste disposal. Bioreinforced materials are attractive and an alternative low-cost substitute and widely available. This chapter deals with the preparation, characterization, and applications of natural polymer blends and their composites in a systematic and detailed way.

1.1 INTRODUCTION

Natural polymers have attracted an increasing attention over the past two decades, mainly due to their abundance and low cost in addition to environmental concerns, and the anticipated depletion of petroleum resources. This has led to a growing interest in developing chemical and biochemical processes to acquire and modify natural polymers, and to utilize their useful inherent properties in a wide range of applications of industrial interests in different fields (Zhao, Jin, Cong, Liu, & Fu, 2013). The development of commodities derived from petrochemical polymers has brought many benefits to mankind. However, it is becoming more evident that the ecosystem is considerably disturbed and damaged as a result of the non-degradable plastic materials used in disposable items. Therefore, the interest in polymers from renewable resources has recently gained exponential momentum and the use of biodegradable and renewable materials to replace conventional petroleum plastics for disposable applications is becoming popular (Yu, Dean, & Li, 2006). Within the broad family of renewable polymers, starch is one of the most attractive and promising sources for biodegradable plastics because of the abundant supply, low cost, renewability, biodegradability, and ease of chemical modifications (Mathew & Dufresne, 2002; Mohanty, Misra, & Hinrichsen, 2000).

Compared to polymeric resources from petroleum, natural polymers from renewable resources have the advantages of biodegradability, biocompatibility, nontoxicity, high reactivity, low cost, ease of availability, and so forth (Mecking, 2004; Smith, 2005; Wool, 2005). They also possess great reinforcing function in composites, similar to traditional inorganic nanofillers (Angellier, Molina-Boisseau, & Dufresne, 2005a; Angellier, Molina-Boisseau, Belgacem, & Dufresne, 2005b; Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Labet, Thielemans, & Dufresne, 2007; Thielemans & Wool, 2005; Yuan, Nishiyama, Wada, & Kuga, 2006), by virtue of their rigidity to form strong physical interactions. Due to the similarity with living tissues, natural polymers are biocompatible and non-cytotoxic (Druchok & Vlachy, 2010; Gentile, Chiono, Carmagnola, & Hatton, 2014; Rutledge, Cheng, Pryzhkova, Harris, & Jabbarzadeh, 2014). A great variety of materials derived from natural sources have been studied and proposed for different biomedical uses (Hietala, Mathew, & Oksman, 2013; Mohanty et. al., 2000). Starch-based polymers present enormous potential for wide use in the biomedical field ranging from bone replacement to engineering of tissue scaffolds and drug-delivery systems (Crépy, Petit, Wirquin, Martin, & Joly, 2014; Maran, Sivakumar, Sridhar, & Immanuel, 2013; Xie, Pollet, Halley, & Avérous, 2013).

1.2 CELLULOSE-BASED BLENDS, COMPOSITES AND NANOCOMPOSITES

Consumers, industry, and government are increasingly demanding products made from renewable and sustainable resources that are biodegradable, non-petroleum based, carbon neutral, and have low environmental, animal/human health and safety risks. Natural cellulose-based materials (wood, hemp, cotton, linen, etc.) have been used by our society as engineering materials for thousands of years and their use continues today as verified by the enormity of the worldwide industries in forest products, paper, textiles, etc. Natural materials develop functionality, flexibility and high mechanical strength/weight performance by exploiting hierarchical structure design that spans nanoscale to macroscopic dimensions.

Cellulose is a linear chain of ringed glucose molecules and has a flat ribbon-like conformation. The intra- and inter-chain hydrogen bonding network makes cellulose a relatively stable polymer. These cellulose fibrils contain both crystalline and amorphous phases, (Fig. 1.1a–c).



FIGURE 1.1 (a) Structure of cellulose monomeric unit; (b) Schematic representations of crystalline and amorphous regions in the cellulose micro fibril; (c) cellulose nanocrystals after acid hydrolysis (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011).

The nanocellulose was prepared mainly by three different techniques, namely mechanical treatment (Hubbe, Rojas, Lucia, & Sain, 2008; Karimi, Tahir, Karimi, Dufresne, & Abdulkhani, 2014; Siró & Plackett, 2010), acid hydrolysis (Habibi, Lucia, & Rojas, 2010; Satyamurthy & Vigneshwaran, 2013; Syverud & Stenius, 2009; Tang, Yang, Zhang, & Zhang, 2014), and enzymatic hydrolysis (Penttilä et al., 2013; Siqueira, Tapin-Lingua, Bras, da Silva Perez, & Dufresne, 2011). Mechanical processes, such as high-pressure homogenizers (Cervin, Aulin, Larsson, & Wågberg, 2012; Li et al., 2012), grinders/refiners (Baheti, Abbasi, & Militky, 2012; Jin et al., 2011; Vartiainen et al., 2011), cryocrushing (Chakraborty, Sain, & Kortschot, 2005), high-intensity ultrasonic treatments (Mishra, Manent, Chabot, & Daneault, 2011; Mishra, Thirree, Manent, Chabot, & Daneault, 2010), and microfluidization (Tanaka, Hjelt, Sneck, & Korpela, 2012; Zhu, Sabo, & Luo, 2011), have been used for removing cellulose fibrils from different source materials. Repeated mechanical treatment leads to the reduction in percentage of cellulose crystallinity due to increased mechanical damage to the crystalline cellulose. For the extraction of nano crystalline cellulose particles from a variety of cellulose sources, acid hydrolysis technique was mainly used. By this technique, the amorphous regions within the cellulose microfibrils were removed. Sulfuric acid is the most typically used acid reagent, as it provides a net negative surface charge on the particles, leading to

more stable suspensions (Mandal & Chakrabarty, 2011; Tang et al., 2014; Jiang & Hsieh, 2013), but other acids have also been used, such as hydrochloric acid (Jiang& Hsieh, 2013; Ludueña, Fasce, Alvarez, & Stefani, 2011), phosphoric acid (Camarero, Kuhnt, Foster, & Weder, 2013), oxalic acid (Abraham et al., 2011; Abraham et al., 2013; Chirayil et al., 2014) etc.

The reason for the use of nanocellulose in reinforced polymer matrix composites processing is that it is desirable to have both, a fine nanocellulose dispersion while also forming a nanocellulose network structure. The research has focused on producing composites with maximized and reproducible properties by developing processing routes that maximize fine nanocellulose dispersion. Four processing techniques have been used to make nanocellulose reinforced polymer matrix composites: solution casting (Azizi, Alloin, & Dufresne, 2005; Habibi et al., 2010; Liu, Sui, & Bhattacharyya, 2014), melt-compounding (Cobut, Sehaqui, & Berglund, 2014; Eichhorn et al., 2010; Hietala et al., Kamel, 2007; 2013; Reddy & Rhim, 2014), partial dissolution and electrospinning (Gabr et al., 2014; Liu, Yuan, & Bhattacharyya, 2012; Peresin et al., 2010; Rojas, Montero, & Habibi, 2009; Zoppe, Peresin, Habibi, Venditti, & Rojas, 2009). In addition to the low cost of the raw material, cellulose has other benefits like low energy consumption; high specific properties, low density; renewable nature, biodegradability; relatively reactive surface, great availability (Espert, Vilaplana, & Karlsson, 2004; Faruk, Bledzki, Fink, & Sain, 2014; Gandini & Belgacem, 2008). High moisture absorption, incompatibility with most polymeric matrices, low wettability, limitations of processing temperature are some limitations of nanocellulose over other fillers (Han, Zhou, Wu, Liu, & Wu, 2013; Wambua, Ivens, & Verpoest, 2003).

Jonoobi et al., has reported a comparative study of modified and unmodified cellulose nanofiber reinforced polylactic acid (PLA) prepared by twin screw extrusion (Jonoobi, Mathew, Abdi, Makinejad, & Oksman, 2012), Liu et al., also reported the characterization of solution cast cellulose nanofiber reinforced poly (lactic acid) (Liu, Yuan, Bhattacharyya, & Easteal, 2010). Fortunati et al. described the effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites (Fortunati et al., 2012). Song et al. reported a work on lowering water vapor transmission rate (WVTR) of paper by the incorporation of hydrophobic modified nanocellulose fiber on PLA biodegradable composites (Song, Xiao, & Zhao, 2014). Correction to transparent nanocellulosic multilayer thin films on polylactic acid with tunable gas barrier properties is described by Aulin, Karabulut, Tran, Wågberg, and Lindström (2013). Nanocellulose is a promising reinforcement for PLA composites.

The nanocellulose from various sources, such as cotton, tunicate, algae, bacteria, ramie, and wood for preparation of high-performance composite materials, have been investigated extensively (Azizi, et. al., 2005). Both natural and synthetic polymers were explored as the matrixes. Natural polymers such as poly (β -hydroxyoctanoate) (PHO) (Dubief, Samain, & Dufresne, 1999), soy protein (Wang, Cao, & Zhang, 2006), silk fibroin (Noishiki, Nishiyama, Wada, Kuga, & Magoshi, 2002) reinforced with cellulose whiskers were reported. Meanwhile, Poly-(styrene-cobutylacrylate) (poly(S-co-BuA)) (Helbert, Cavaille, & Dufresne, 1996), poly (vinyl chlo-ride) (PVC) (Chazeau, Cavaille, Canova, Dendievel, & Boutherin, 1999), polypropylene (Ljungberg et al., 2005), waterborne polyurethane (Cao, Dong, & Li, 2007), were also used as synthetic matrixes.

1.3 STARCH-BASED BLENDS, COMPOSITES AND NANOCOMPOSITES

Starch from a variety of crops such as corn, wheat, rice and a potato is a source of biodegradable plastics, which are readily available at low cost when compared with most synthetic plastics (Ma, Chang, & Yu, 2008a). Starch is comprised of amylose, a linear polymer with molecular weight between 103 and 106 and amylopectin, a branched polymer with a-(1-6)-linked branch points (Fig. 1.2a–b) (Dufresne & Vignon, 1998).



FIGURE 1.2 (a-b) Structure of amylose and amylopectin

In the glassy state, starch tends to be brittle and is very sensitive to moisture. In order to extrude or mold an object from starch, it is often converted into a thermoplastic starch (TPS) (Dufresne, Dupeyre, & Vignon, 2000). Both native starch and TPS can suffer from poor mechanical properties and high-water uptake compared to conventional polymers. Moreover, these properties may change after processing (Averous, 2004; Ma, Chang, Wang, & Yu, 2008b). Micro cellulose fiber and bacterial cellulose have also been reported as promising candidates for starch reinforce-

ment. Dufresne et al. (2000) aimed to improve the thermomechanical properties and reduce the water sensitivity of potato starch-based nanocomposites, while preserving the biodegradability of the material through addition of Micro cellulose. This significantly reinforced the starch matrix, regardless of the plasticizer content, and the increase in tensile modulus as a function of filler content was almost linear.

1.4 CHITIN AND CHITOSAN-BASED BLENDS, COMPOSITES AND NANOCOMPOSITES

Chitin, poly (β -(1-4)-N-acetyl-d-glucosamine), is a natural polysaccharide of major importance, first identified in 1884. Chitin occurs in nature as ordered crystalline microfibrils forming structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast. It is also produced by a number of other living organisms in the lower plant and animal kingdoms, serving in many functions where reinforcement and strength are required. The most important derivative of chitin is chitosan (Fig. 1.3), obtained by (partial) deacetylation of chitin in the solid state under alkaline conditions (concentrated NaOH) or by enzymatic hydrolysis in the presence of chitin deacetylase. Because of the semicrystalline morphology of chitin, chitosan obtained by solid-state reaction has a heterogeneous distribution of acetyl groups along the chains.



FIGURE 1.3 Structure of chitin and chitosan

Among the natural polymers, chitosan occupies a special position due to its abundance, versatility, facile modification, and unique properties, including biodegradability (Kean & Thanou, 2010), biocompatibility (Costa-Pinto et al., 2014; Hsu

et al., 2011; Shi et al., 2012), non-toxicity (Stephen-Haynes, Gibson, & Greenwood, 2014), and anti-bacterial (Adila, Suyatma, Firlievanti, & Bujang, 2013; Champer et al., 2013; Kong, Chen, Xing, & Park, 2010), as well as, hydrophilicity (Xiao, Gao, & Gao, 2010). Chitin and chitosan are biocompatible, biodegradable, and non-toxic polymers (Anitha et al., 2014). This has made chitosan a very useful compound in a wide range of applications in medical, pharmaceutical, chemical, agricultural, and environmental fields (Croisier & Jérôme, 2013). Due to its non-toxicity, it can be applied in the food industry. Chitosan is also biocompatible and antibacterial, with wound-healing effects. Therefore, it can play a role in various medical applications (Croisier & Jérôme, 2013; Dash, Chiellini, Ottenbrite, & Chiellini, 2011; Huang, 2011; Jayakumar, Prabaharan, Sudheesh Kumar, Nair, & Tamura, 2011; Jayakumar, Menon, Manzoor, Nair, & Tamura, 2010a; Jayakumar, Prabaharan, Nair, & Tamura, 2010b; Larsson et al., 2013; Silva et al., 2013; Stephen-Haynes et al., 2014). This is due to its capability of binding a high amount of fats (about 4 to 5 times its weight) compared to other fibers. Chitosan is safely used in the field of agriculture for controlled agrochemical release, seed coating and making fertilizer due to its biodegradability and natural origin (Dzung, Khanh, & Dzung, 2011; El-Sawy, Abd El-Rehim, Elbarbary, & Hegazy, 2010; Zeng & Luo, 2012). In environmental applications, chitosan plays an important role in wastewater treatment and industrial toxic pollution management as it has the ability to adsorb dyes, pesticides, and toxic metals from water and waste water (Altaher, 2012; Chen, Chen, Bai, & Li, 2013; DelaiáSun, 2011). Blending of chitosan with other biopolymers has been proposed as an interesting method to obtain new biomaterials with enhanced properties to meet the requirements of specific applications.

1.5 LIGNIN-BASED BLENDS, COMPOSITES AND NANOCOMPOSITES

Lignin, after cellulose, is the second-most abundant polymer on the planet. Lignin has a complex and non-uniform structure with aliphatic and aromatic constituents. It consists of phenylpropanoid units having various substituent functional groups (Fig. 1.4). Depending on the plant species the structure of lignin may vary by botanical origin, growing conditions of the original plant, extraction conditions, etc. It has a cross-linked structure with many different chemical groups. Its intricate chemical structure has been studied using fragmentation methods. The main precursors are three aromatic alcohols, namely p-coumaryl, coniferyl and sinapyl alcohols, which undergo cross linking and give rise to the complex structure of lignin (Buranov & Mazza, 2008; Floudas et al., 2012; Martínez et al., 2010).



FIGURE 1.4 Structure of lignin

Lignin is more reactive than cellulose and other natural polymers due to the presence of specific functional groups. Studies conducted on the reactivity of functional groups of the biopolymer, as well as its modification, have facilitated a succession of new methods of application in various industries. Due to its structure, lignin has been investigated as compatibilizer and as an antioxidant. Its utilization as compatibilizer is justified by the presence of both aliphatic and polar groups, which may provide compatibility between nonpolar polymers and lignocellulosic fibers (Fig. 1.4) (Gregorová, Cibulková, Kosiková, & Simon, 2005; Guigo, Vincent, Mija, Naegele, & Sbirrazzuoli, 2009; Morandim-Giannetti et al., 2012).

More than 70 million tons of lignin per year are generated as a residue of chemical pulping (Monteil-Rivera, Phuong, Ye, Halasz, & Hawari, 2013). Among the different available processes for extracting lignin from vegetal sources, organosolv and kraft pulping processes are particularly relevant. There are several methods for extracting lignin from lignocellulosic materials (Thakur, Thakur, Raghavan, & Kessler, 2014; Yuan, Xu, & Sun, 2013). However, the structure of natural lignin is not preserved in any of these techniques, because delignification involves the breaking of covalent bonds in natural lignin. Lignin is extracted with an organic solvent and water, usually in the presence of an acid catalyst. Advantages are that such lignin has a low molecular weight when compared to lignin obtained from other processes and contains many reactive sites available for functionalization (Faulstich de Paiva & Frollini, 2006; Oliveira, Marcia, Favaro, & Vale, 2013; Ramires, de Oliveira, & Frollini, 2013). On the other hand, kraft pulping is the most-used delignification process in the paper and cellulose industries (Novikova, Medvedeva, Volchatova, & Bogatyreva, 2002; Thielemans & Wool, 2005; Thunga, Chen, Grewell, & Kessler, 2014). Kraft lignin is a polydispersed, branched, biopolymer of high molecular weight. Finally, hydrolytic lignin is a heterogeneous product of acidic wood processing, which is composed of lignin itself (up to 88%), poly and monosaccharide residues, organic acids, resins, waxes, nitrogenous compounds, ashes and mineral acids that are not washed out after wood hydrolysis (Novikova et al., 2002).

1.6 CONCLUSIONS

The strategy discussed in this chapter aims to discuss the natural polymer-based blends, composites, and its applications. One of the other major environmental problems is the plastic waste disposal. The tremendous production of plastics and its use in every segment of our life has increased the plastic waste to huge quantities. The growing global environmental and social concern, high rate of depletion of petroleum resources, and new environmental regulations have forced the search for new composites and green materials, compatible with the environment. The research field of biodegradable polymers is still in its early stages, but is growing in popularity every day. Currently, a lot of polymer biodegradable matrices have appeared as commercial products, offered by various producers. The future outlook for development in the field of biopolymers material is promising because of its eco friendly behavior. Bio-composites often lead to the fabrication of light weight and low-cost materials having potential applications in the fields of environmental protection and the maintenance of physical health.

KEYWORDS

- polymer blend
- polymer composites
- cellulose
- chitosan
- chitin
- starch
- lignin

REFERENCES

- Abraham, E., Deepa, B., Pothan, L. A., Jacob, M., Thomas, S., Cvelbar, U., & Anandjiwala, R. (2011). Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach. (4), 1468–1475.
- Abraham, E., Deepa, B., Pothen, L. A., Cintil, J., Thomas, S., John, M. J., & Narine, S. S. (2013). Environmental friendly method for the extraction of coir fibre and isolation of nanofiber. (2), 1477–1483.
- Adila, S. N., Suyatma, N. E., Firlieyanti, A. S., & Bujang, A. (2013). Antimicrobial and physical properties of Chitosan film as affected by solvent types and glycerol as plasticizer. , 155–159.
- Altaher, H. (2012). The use of chitosan as a coagulant in the pre-treatment of turbid sea water. , 97-102.
- Angellier, H., Molina-Boisseau, S., & Dufresne, A. (2005a). Mechanical properties of waxy maize starch nanocrystal reinforced natural rubber. (22), 9161–9170.
- Angellier, H., Molina-Boisseau, S., Belgacem, M. N., & Dufresne, A. (2005b). Surface chemical modification of waxy maize starch nanocrystals. (6), 2425–2433.
- Angellier, H., Molina-Boisseau, S., Dole, P., & Dufresne, A. (2006). Thermoplastic starch-waxy maize starch nanocrystals nanocomposites. (2), 531–539.
- Anitha, A., Sowmya, S., Kumar, P. T., Deepthi, S., Chennazhi, K. P., Ehrlich, H., ... & Jayakumar, R. (2014). Chitin and chitosan in selected biomedical applications.
- Aral, C., & Akbuğa, J. (1998). Alternative approach to the preparation of chitosan beads. (1), 9–15.
- Aulin, C., Karabulut, E., Tran, A., Wågberg, L., & Lindström, T. (2013). Correction to transparent nanocellulosic multilayer thin films on polylactic acid with tunable gas barrier properties. ACS (20), 10395–10396.
- Averous, L. (2004). Biodegradable multiphase systems based on plasticized starch: A review. , 231–274.
- Azizi Samir, M. A. S., Alloin, F., & Dufresne, A. (2005). Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. (2), 612–626.
- Baheti, V. K., Abbasi, R., & Militky, J. (2012). Ball milling of jute fibre wastes to prepare nanocellulose. 9(1), 45–50.
- Buranov, A. U., & Mazza, G. (2008). Lignin in straw of herbaceous crops. (3), 237-259.

- Camarero, E. S., Kuhnt, T., Foster, E. J., & Weder, C. (2013). Isolation of thermally stable cellulose nanocrystals by phosphoric acid hydrolysis. 14(4), 1223–1230.
- Cao, X., Dong, H., & Li, C. M. (2007). New nanocomposite materials reinforced with flax cellulose nanocrystals in waterborne polyurethane. (3), 899–904.
- Cervin, N. T., Aulin, C., Larsson, P. T., & Wågberg, L. (2012). Ultra porous nanocellulose aerogels as separation medium for mixtures of oil/water liquids. 19(2), 401–410.
- Chakraborty, A., Sain, M., & Kortschot, M. (2005). Cellulose microfibrils: A novel method of preparation using high shear refining and cryocrushing. 59(1), 102–107.
- Champer, J., Patel, J., Fernando, N., Salehi, E., Wong, V., & Kim, J. (2013). Chitosan against cutaneous pathogens. (1), 37.
- Chazeau, L., Cavaille, J. Y., Canova, G., Dendievel, R., & Boutherin, B. (1999). Viscoelastic properties of plasticized PVC reinforced with cellulose whiskers. (11), 1797–1808.
- Chen, Y., Chen, L., Bai, H., & Li, L. (2013). Graphene oxide-chitosan composite hydrogels as broad-spectrum adsorbents for water purification. (6), 1992–2001.
- Chirayil, C. J., Joy, J., Mathew, L., Mozetic, M., Koetz, J., & Thomas, S. (2014). Isolation and characterization of cellulose nanofibrils from plant. , 27–34.
- Cobut, A., Sehaqui, H., & Berglund, L. A. (2014). Cellulose nanocomposites by melt compounding of TEMPO-treated wood fibers in thermoplastic starch matrix. 9(2), 3276–3289.
- Costa-Pinto, A. R., Martins, A. M., Castelhano-Carlos, M. J., Correlo, V. M., Sol, P. C., Longatto-Filho, A., & Neves, N. M. (2014). In vitro degradation and in vivo biocompatibility of chitosanpoly (butylene succinate) fiber mesh scaffolds. (2), 137–151.
- Crépy, L., Petit, J.-Y., Wirquin, E., Martin, P., & Joly, N. (2014). Synthesis and evaluation of starchbased polymers as potential dispersants in cement pastes and self leveling compounds. , 29–38.
- Croisier, F., & Jérôme, C. (2013). Chitosan-based biomaterials for tissue engineering. (4), 780– 792.
- Dash, M., Chiellini, F., Ottenbrite, R. M., & Chiellini, E. (2011). Chitosan—A versatile semisynthetic polymer in biomedical applications. (8), 981–1014.
- de Oliveira Taipina, M., Ferrarezi, M. M. F., Yoshida, I. V. P., & do Carmo Gonçalves, M. (2013). Surface modification of cotton nanocrystals with a silane agent. (1), 217–226.
- DelaiáSun, D. (2011). Facile fabrication of porous chitosan/TiO 2/Fe 3 O 4 microspheres with multifunction for water purifications. 35(1), 137–140.
- Druchok, M., & Vlachy, V. (2010). Molecular dynamics study of the hydrophobic 6,6-ionene oligocation in aqueous solution with sodium halides. (10), 1943–1955. 13p.
- Dubief, D., Samain, E., & Dufresne, A. (1999). Polysaccharide microcrystals reinforced amorphous poly (β-hydroxyoctanoate) nanocomposite materials. (18), 5765–5771.
- Dufresne, A. & Vignon, M. R. (1998). Improvement of starch film performances using cellulose microfibrils. , 2693–2696.
- Dufresne, A., Dupeyre, D. & Vignon, M. R. (2000). Cellulose microfibrils from potato tuber cells: Processing and characterization of starch-cellulose microfibril composites. (14), 2080–2092.
- Dzung, N. A., Khanh, V. T. P., & Dzung, T. T. (2011). Research on impact of chitosan oligomers on biophysical characteristics, growth, development and drought resistance of coffee. (2), 751–755.
- Eichhorn, S. J., Dufresne, A., Aranguren, M., Marcovich, N. E., Capadona, J. R., Rowan, S. J., ... & Peijs, T. (2010). Review: Current international research into cellulose nanofibres and nanocomposites. (1), 1–33.

- El-Sawy, N. M., Abd El-Rehim, H. A., Elbarbary, A. M., & Hegazy, E. S. A. (2010). Radiationinduced degradation of chitosan for possible use as a growth promoter in agricultural purposes. (3), 555–562.
- Espert, A., Vilaplana, F., & Karlsson, S. (2004). Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. (11), 1267–1276.
- Faruk, O., Bledzki, A. K., Fink, H. P., & Sain, M. (2014). Progress Report on Natural Fiber Reinforced Composites. (1), 9–26.
- Faulstich de Paiva, J. M., & Frollini, E. (2006). Unmodified and modified surface Sisal fibers as reinforcement of phenolic and lignophenolic matrices composites: Thermal analyses of fibers and composites. (4), 405–417.
- Floudas, D., Binder, M., Riley, R., Barry, K., Blanchette, R. A., Henrissat, B., ... & Patyshakuliyeva, A. (2012). The Paleozoic origin of enzymatic lignin decomposition reconstructed from 31 fungal genomes. (6089), 1715–1719.
- Fortunati, E., Peltzer, M., Armentano, I., Torre, L., Jiménez, A., & Kenny, J. M. (2012). Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. (2), 948–956.
- Gabr, M. H., Phong, N. T., Okubo, K., Uzawa, K., Kimpara, I., & Fujii, T. (2014). Thermal and mechanical properties of electrospun nano-celullose reinforced epoxy nanocomposites. , 51–58.
- Gandini, A., & Belgacem, M. N. (2008). Chemical Modification of Wood. In Monomers, Polymers and Composites from Renewable Resources, 1st ed.; Gandini, A., Belgacem, M. N., Eds.; Elsevier: Oxford, UK, 419–432.
- Gentile, P., Chiono, V., Carmagnola, I., & Hatton, P. V. (2014). An overview of poly(lactic-coglycolic) acid (PLGA)-based biomaterials for bone tissue engineering. (3), 3640–59.
- Gregorová, A., Cibulková, Z., Kosiková, B., & Simon, P. (2005). Stabilization effect of lignin in polypropylene and recycled polypropylene. , 553–558.
- Guigo, N., Vincent, L., Mija, A., Naegele, H., & Sbirrazzuoli, N. (2009). Innovative green nanocomposites based on silicate clays/lignin/natural fibres. (11), 1979–1984.
- Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose nanocrystals: Chemistry, self-assembly, and applications. (6), 3479–3500.
- Han, J., Zhou, C., Wu, Y., Liu, F., & Wu, Q. (2013). Self-assembling behavior of cellulose nanoparticles during freeze-drying: Effect of suspension concentration, particle size, crystal structure, and surface charge. (5), 1529–1540.
- Helbert, W., Cavaille, J. Y., & Dufresne, A. (1996). Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: Processing and mechanical behavior. (4), 604–611.
- Hietala, M., Mathew, A. P., & Oksman, K. (2013). Bionanocomposites of thermoplastic starch and cellulose nanofibers manufactured using twin-screw extrusion. , (4), 950–956.
- Hsu, S. H., Chang, Y. B., Tsai, C. L., Fu, K. Y., Wang, S. H., & Tseng, H. J. (2011). Characterization and biocompatibility of chitosan nanocomposites. (2), 198–206.
- Huang, J. (2011). New waterborne polyurethane-based nanocomposites reinforced with low loading levels of chitin whisker. (4), 362–373.
- Hubbe, M. A., Rojas, O. J., Lucia, L. A., & Sain, M. (2008). Cellulosic nanocomposites: A review. (3), 929–980.
- Jayakumar, R., Menon, D., Manzoor, K., Nair, S. V., & Tamura, H. (2010a). Biomedical applications of chitin and chitosan-based nanomaterials—A short review (2), 227–232.

- Jayakumar, R., Prabaharan, M., Nair, S. V., & Tamura, H. (2010b). Novel chitin and chitosan nanofibers in biomedical applications. (1), 142–150.
- Jayakumar, R., Prabaharan, M., Sudheesh Kumar, P. T., Nair, S. V., & Tamura, H. (2011). Biomaterials based on chitin and chitosan in wound dressing applications. (3), 322–337.
- Jiang, F., & Hsieh, Y. L. (2013). Chemically and mechanically isolated nanocellulose and their self-assembled structures. (1), 32–40.
- Jin, H., Kettunen, M., Laiho, A., Pynnönen, H., Paltakari, J., Marmur, A., & Ras, R. H. (2011). Superhydrophobic and superoleophobic nanocellulose aerogel membranes as bioinspired cargo carriers on water and oil. (5), 1930–1934.
- Jonoobi, M., Harun, J., Mathew, A. P., & Oksman, K. (2010). Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. (12), 1742–1747.
- Jonoobi, M., Mathew, A. P., Abdi, M. M., Makinejad, M. D., & Oksman, K. (2012). A comparison of modified and unmodified cellulose nanofiber reinforced polylactic acid (PLA) prepared by twin screw extrusion. (4), 991–997.
- Kamel, S. (2007). Nanotechnology and its applications in lignocellulosic composites, a mini review. , (9), 546–575.
- Karimi, S., Tahir, P. M., Karimi, A., Dufresne, A., & Abdulkhani, A. (2014). Kenaf bast cellulosic fibers hierarchy: A comprehensive approach from micro to nano. , 878–885.
- Kean, T., & Thanou, M. (2010). Biodegradation, biodistribution and toxicity of chitosan. (1), 3-11.
- Kong, M., Chen, X. G., Xing, K., & Park, H. J. (2010). Antimicrobial properties of chitosan and mode of action: A state of the art review. (1), 51–63.
- Labet, M., Thielemans, W., & Dufresne, A. (2007). Polymer grafting onto starch nanocrystals. , (9), 2916–2927.
- Larsson, M., Huang, W. C., Hsiao, M. H., Wang, Y. J., Nydén, M., Chiou, S. H., & Liu, D. M. (2013). Biomedical applications and colloidal properties of amphiphilically modified chitosan hybrids. e, 38(9), 1307–1328.
- Li, J., Wei, X., Wang, Q., Chen, J., Chang, G., Kong, L., & Liu, Y. (2012). Homogeneous isolation of nanocellulose from sugarcane bagasse by high pressure homogenization. , (4), 1609–1613.
- Liu, D. Y., Sui, G. X., & Bhattacharyya, D. (2014). Synthesis and characterisation of nanocellulose-based polyaniline conducting films. , 31–36.
- Liu, D. Y., Yuan, X. W., Bhattacharyya, D., & Easteal, A. J. (2010). Characterisation of solution cast cellulose nanofiber—reinforced poly (lactic acid). (1), 26–31.
- Liu, D., Yuan, X., & Bhattacharyya, D. (2012). The effects of cellulose nanowhiskers on electrospun poly (lactic acid) nanofibers (7), 3159–3165.
- Ljungberg, N., Bonini, C., Bortolussi, F., Boisson, C., Heux, L., & Cavaillé, J. Y. (2005). New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: Affect of surface and dispersion characteristics. , (5), 2732–2739.
- Ludueña, L., Fasce, D., Alvarez, V. A., & Stefani, P. M. (2011). Nanocellulose from rice husk following alkaline treatment to remove silica. (2), 1440–1453.
- Ma, X. F., Chang, P. R. & Yu, J. G. (2008a). Properties of biodegradable thermoplastic pea starch/ carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. , 369–375.
- Ma, X. F., Chang, P. R., Yu, J. G. & Wang, N. (2008b). Preparation and properties of biodegradable poly(propylene carbonate)/thermoplastic dried starch composites. , 229–234.

- Mandal, A., & Chakrabarty, D. (2011). Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. (3), 1291–1299.
- Maran, J. P., Sivakumar, V., Sridhar, R., & Immanuel, V. P. (2013). Development of model for mechanical properties of tapioca starch-based edible films. , (Complete), 159–168.
- Martínez, Á. T., Speranza, M., Ruiz-Dueñas, F. J., Ferreira, P., Camarero, S., Guillén, F., ... & del Río, J. C. (2010). Biodegradation of lignocellulosics: Microbial, chemical, and enzymatic aspects of the fungal attack of lignin. (3), 195–204.
- Mathew, A. P., & Dufresne, A. (2002). Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. , (3), 609–617.
- Mecking, S. (2004). Nature or petrochemistry?—biologically degradable materials. , (9), 1078–1085.
- Mishra, S. P., Manent, A. S., Chabot, B., & Daneault, C. (2011). Production of nanocellulose from native cellulose-various options utilizing ultrasound. (1), 0422–0436.
- Mishra, S. P., Thirree, J., Manent, A. S., Chabot, B., & Daneault, C. (2010). Ultrasound-catalyzed TEMPO-mediated oxidation of native cellulose for the production of nanocellulose: Effect of process variables. (1), 121–143.
- Mohanty, A. K., Misra, M., & Hinrichsen, G. (2000). Biofibres, biodegradable polymers and biocomposites: An overview. , (1), 1–24.
- Monteil-Rivera, F., Phuong, M., Ye, M., Halasz, A., & Hawari, J. (2013). Isolation and characterization of herbaceous lignins for applications in biomaterials. , 356–364.
- Moon, R. J., Martini, A., Nairn, J., Simonsen, J., & Youngblood, J. (2011). Cellulose nanomaterials review: Structure, properties and nanocomposites. (7), 3941–3994.
- Morandim-Giannetti, A. A., Agnelli, J. A. M., Lanças, B. Z., Magnabosco, R., Casarin, S. A., & Bettini, S. H. (2012). Lignin as additive in polypropylene/coir composites: Thermal, mechanical and morphological properties. (4), 2563–2568.
- Muzzarelli, R. A., Boudrant, J., Meyer, D., Manno, N., DeMarchis, M., & Paoletti, M. G. (2012). Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: A tribute to Henri Braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial., (2), 995–1012.
- Noishiki, Y., Nishiyama, Y., Wada, M., Kuga, S., & Magoshi, J. (2002). Mechanical properties of silk fibroin–microcrystalline cellulose composite films. , (13), 3425–3429.
- Novikova, L. N., Medvedeva, S. A., Volchatova, I. V., & Bogatyreva, S. A. (2002). Changes in macromolecular characteristics and biological activity of hydrolytic lignin in the course of composting., (2), 181–185.
- Penttilä, P. A., Várnai, A., Pere, J., Tammelin, T., Salmén, L., Siika-aho, M., & Serimaa, R. (2013). Xylan as limiting factor in enzymatic hydrolysis of nanocellulose. , 135–141.
- Peresin, M. S., Habibi, Y., Vesterinen, A. H., Rojas, O. J., Pawlak, J. J., & Seppälä, J. V. (2010). Effect of moisture on electrospun nanofiber composites of poly (vinyl alcohol) and cellulose nanocrystals. (9), 2471–2477.
- Ramires, E. C., de Oliveira, F., & Frollini, E. (2013). Composites based on renewable materials: Polyurethane-type matrices from forest byproduct/vegetable oil and reinforced with lignocellulosic fibers., (4), 2224–2233.
- Reddy, J. P., & Rhim, J. W. (2014). Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose. , 480–488.
- Rojas, O. J., Montero, G. A., & Habibi, Y. (2009). Electrospun nanocomposites from polystyrene loaded with cellulose nanowhiskers. (2), 927–935.