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Enhancing mechanical properties of polylactic acid through the incorporation of cellulose nanocrystals for engineering plastic applications

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Abstract: This study investigates the potential of enhancing the mechanical properties of polylactic acid (PLA) using cellulose nanocrystals (CNC). Recognized for their high specific strength and stiffness, CNCs are considered to improve the performance of PLA in engineering plastic applications. The synthesis involves a twin-screw extrusion process, which facilitates the uniform dispersion of CNC within the PLA matrix. The mechanical properties, including tensile strength and elongation at break, are comprehensively analyzed, highlighting the effects of CNC concentrations on the performance of PLA composites. Notably, the addition of 1 wt% CNC resulted in a 20% increase in strain at break compared to pure PLA, demonstrating enhanced ductility. Additionally, the thermal resistance of the composite increased by 0.3% with the inclusion of 5 wt% CNC. This study highlights the positive effect of CNC addition on the mechanical properties of PLA composites, making them more suitable for specialized engineering uses.

Keywords: Polylactic acid; Cellulose nanocrystals; Mechanical properties; Biocomposites, Engineering plastics

1. Introduction

Annually, 11 million metric tons of plastic are added to the staggering 200 million metric tons circulating in our oceans [1]. From stray plastic bags and straws finding their way into gutters to vast volumes of improperly managed plastic waste from booming economies, this is equivalent to dumping the contents of a New York City garbage truck into the ocean every single minute of the year. Such an immense accumulation of plastic significantly affects ocean ecosystems. In recent years, biodegradable polymers have gained significant attention in research and industry applications worldwide, with cellulose [2], [3], [4], [5], chitosan [6], [7], PVA [8], [9], [10], and polylactic acid (PLA) particularly notable. Compared to conventional plastics, biodegradable plastics can decompose up to 90% within three to six months in a composting environment, ultimately breaking into water and carbon dioxide and returning to nature. These materials dramatically reduce the environmental burden of plastic pollution. However, these polymers generally have lower mechanical properties and thermal resistance, making their processing parameters more challenging to control, and they are also more expensive than traditional plastics, limiting their application and development.

Therefore, nanocellulose extracted from natural plants has been extensively studied to enhance the mechanical and tribological properties of biodegradable polymers [11], [12]. Cellulose is the world's most abundant renewable resource, with an annual production of 830 million metric tons through photosynthesis [13]. This surge in research is driven by factors such as fossil fuel scarcity, rising costs, the growing awareness of environmental protection, and the rise of the green energy sector [14], [15], [16], [17], [18], [19]. As a biodegradable material, cellulose offers an eco-friendly alternative to synthetic materials, helping to reduce pollution and reliance on fossil fuels [20], [21]. In addition to its use in producing biofuels as a sustainable energy source and serving as an efficient adsorbent in water treatment, cellulose finds applications in the biomedical field, including drug delivery systems and tissue engineering scaffolds [22], [23], [24].

The application of PLA has also continued to evolve, starting in the early 1980s with the first generation aimed at human organ repair materials, such as surgical sutures and scaffolds for tissue engineering [25], [26], [27], [28], [29]. As environmental awareness increased, the second generation of PLA began in the early 2000s and aimed to replace ordinary plastics in short-term-use products and disposable packaging applications. This study hypothesizes that utilizing cellulose nanocrystals (CNC), known for their superior specific strength and stiffness, can enhance the mechanical properties of polylactic acid (PLA) to engineer plastic applications.

2. Material dan methods

Polylactic acid (PLA) is a thermoplastic aliphatic polyester derived from renewable resources, such as corn starch. This study utilized extrusion-grade PLA polymer (Ingeo™ biopolymer 2003D from NatureWorks LLC). Nanocrystalline celluloses (CNCs) are rod-like or whisker-shaped particles obtained through the acid hydrolysis of sources like wheat flour, pea starch, and various forms of cellulose. CNC powder, provided by CelluForce (product name: CelluForce NCC™), was employed to enhance the PLA's mechanical properties and thermal stability.

The nanocrystalline cellulose (CNC)/polylactic acid (PLA) biocomposite material was synthesized using twin-screw extrusion. Following extrusion, injection molding was employed to fabricate test specimens following ASTM standards. The study evaluated the impact of extrusion temperature on the thermal degradation nanofillers distribution of the CNC/PLA composite. The mechanical and thermal properties of the composites, containing varying amounts of nanocrystalline cellulose (1, 3, 5 wt.%), were investigated. Surface morphology was observed using a Scanning Electron Microscope (SEM). The mechanical properties were measured using a standard tensile testing machine (QC-H51A2) following ASTM D 638 Type I specifications. Adhesive shear strength was determined based on the ASTM D5868 standard. The thermal properties of the composite materials were analyzed using Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) with a Perkin Elmer DSC6000 instrument. All the graphs in the figures were prepared by using Origin Software.

3. Results and discussion

3.1 Mechanical and thermal properties

Figure 1 displays the results of the tensile tests, including yield strength, tensile strength, Young's modulus, and elongation at break. This study recorded the yield strength, Young's modulus (E), and elongation at break for pure PLA as 61.3 MPa, 3.2 GPa, and 3.82%, respectively. Research by M. Jonoobi et al. on PLA composites with CNC, pure PLA's mechanical properties after blending were 58.9 ± 0.5 MPa, 2.9 ± 0.6 GPa, and 3.4 ± 0.4% [30]. Tensile results by D. Bondeson and K. Oksman indicated that pure PLA had a yield strength of 62.8 ± 1.0 MPa, Young's modulus of 2.65 ± 0.08 GPa, and an elongation at break of 19.5 ± 9.7% [31]. These variations in yield strength were not due to experimental error but were attributed to the influence of processing parameters during blending, as the polymer molecular weight typically decreased slightly after screw shear action, thereby affecting mechanical properties.

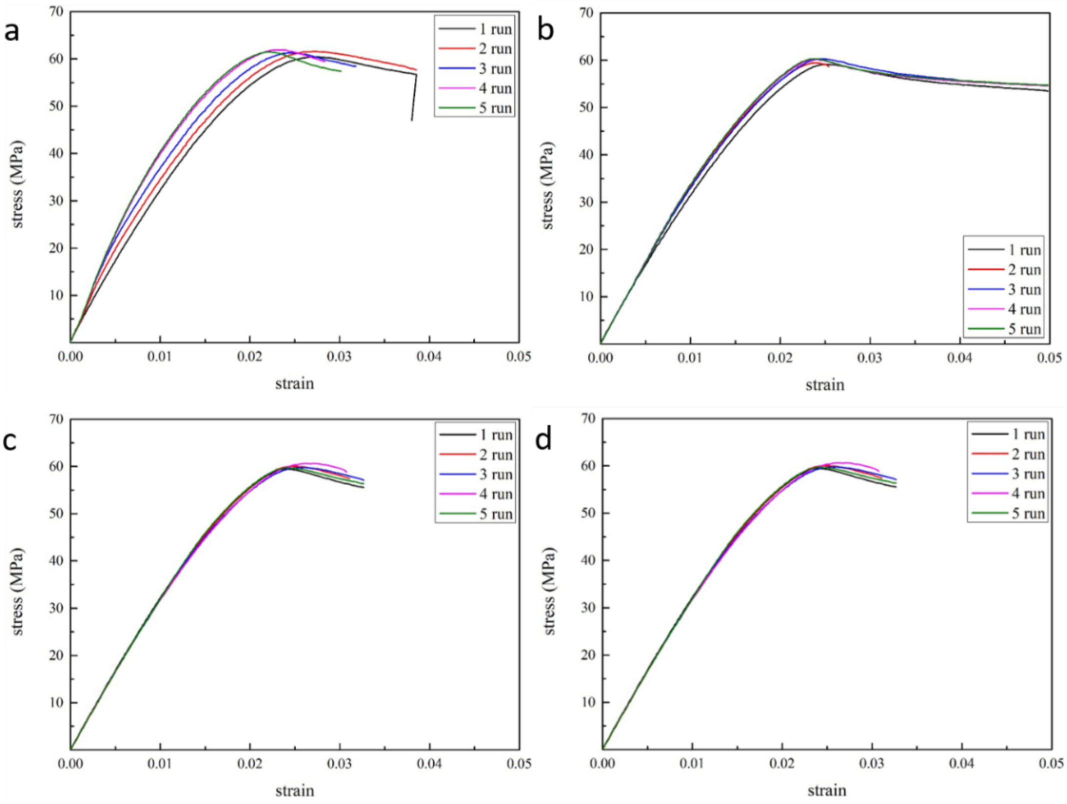

Figure 1 Stress-strain curves of the composite material (a) Pure PLA, (b) 1 wt% CNC/PLA, (c) 3 wt% CNC/PLA, (d) 5 wt% CNC/PLA

Additionally, experimental results indicated that yield strength (σ_y) and elongation at break slightly decreased as the CNC content increased. In contrast, Young's modulus (E) and tensile strength (σ_B) increased, suggesting that the composite became more rigid and brittle. E. Fortunati et al. observed that reduced elongation at break when adding cellulose to polymers is a common trend in thermoplastic composites due to the interactions between the additive and the PLA matrix [32].

Moreover, the experiments demonstrated that the yield strength did not increase with higher CNC content because of the aggregation of CNC, which created porosity and defects among PLA molecules. CNC underwent aggregation twice: firstly, commercial CNCs are typically prepared using spray drying, causing aggregation into approximately 10-20 μm particles due to hydrogen bonding. Y. Strong hydrogen bonding among CNCs promoted re-aggregation during the spray drying process, as evidenced by the rough surface texture of CNC samples obtained, which was caused by CNC aggregation [33]. Secondly, aggregation occurred again during twin-screw blending, that pointed out that although CNCs improved the mechanical properties of PLA, poor dispersion within PLA during melt blending led to further aggregation [15]. Hypothesized that even with modified CNCs at high concentrations, uneven dispersion could be attributed to insufficient shearing or short residence time in the twin-screw mixer; even changing the screw configuration before blending to promote uniform dispersion achieved limited success [34].

Compared to the maximum tensile strengths of phenolics and nylon, the experiment found that the tensile strength of PLA gradually decreased with increasing CNC content. According to American Gear Manufactures Association (AGMA) standards for the minimum tensile strength of plastic gears at 10,000 MPa, PLA's maximum tensile strength was only 9427 psi, which is 20.9% lower than the recommended minimum, as shown in Figure 2.

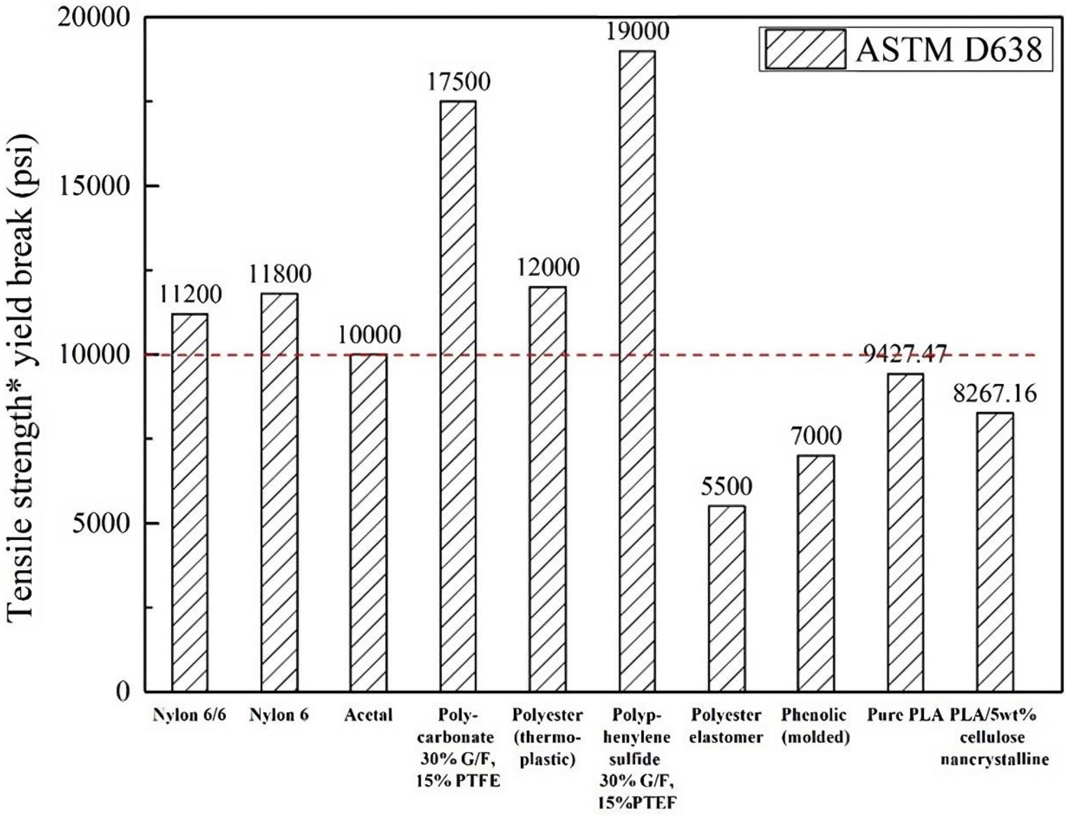

Figure 2. Comparison of tensile strength between commercially available engineering materials and pure PLA and PLA/CNC composites

3.2 Tensile fracture surface analysis

Figure 3 depicts the tensile fracture surfaces of pure PLA and PLA composites with 1, 3, and 5 wt.% CNC, analyzed through SEM to demonstrate the influence of CNC on fracture behavior and its compatibility with the polymer matrix. As shown in Figure 4.10(a), pure PLA, being a rigid material, exhibited a typical brittle fracture morphology with extensive fracture planes, indicating that the fracture surface of pure PLA did not show significant plastic deformation, which is associated with its low energy absorption capacity [35], [36], [37]. This crack formation was due to the deformation of the PLA matrix, and it highlights the enhancement of toughness attributed to increased resistance to deformation, leading to higher energy absorption. It is important to note that the interactions between the filler and the matrix (such as adhesion between the substrate and the filler, filler size, and concentration) can either enhance or deteriorate mechanical properties [36].

It was, compared to the 1 wt% CNC content, the fracture surfaces for 3 wt.% and 5 wt.% CNC was more irregular and relatively rougher [31], indicating a lack of tough tearing and revealing more voids. This phenomenon suggests that CNC content exceeding 1 wt.% led to severe aggregation, resulting in phase separation between the PLA matrix and CNC. The tensile results from Table 4.3 corroborate this, where the elongation at break increased from 3.82% to 4.41% at 1 wt.% CNC content but drastically decreased as the content rose to 5 wt.%, confirming severe aggregation at 3 wt.% and 5 wt.% CNC.

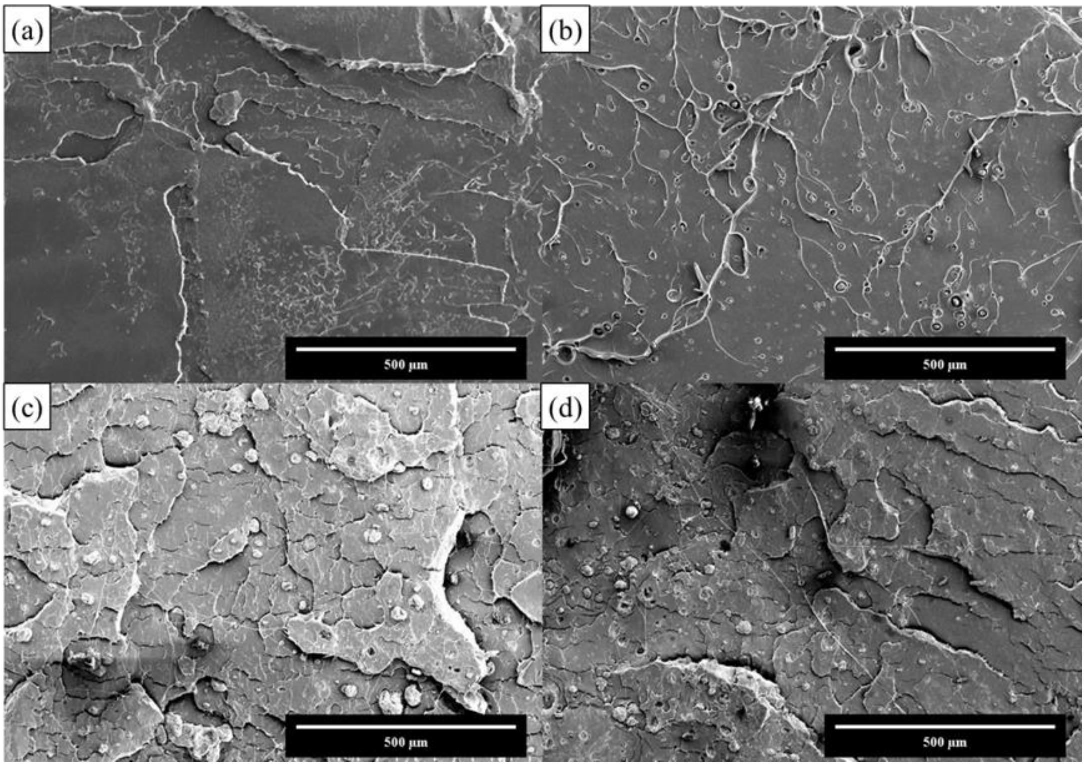

Figure 3. Tensile fracture surfaces (a) Pure PLA, (b) 1 wt% CNC/PLA, (c) 3 wt% CNC/PLA, (d) 5 wt% CNC/PLA

3.3 Thermal behavior of CNC/PLA composite: TGA and DSC

Thermogravimetric Analysis (TGA) demonstrated the effects of twin-screw blending on PLA's degradation temperature and the impact of incorporating 1, 3, and 5 wt% CNC. The onset and maximum degradation temperatures were observed, as shown in Figure 4a. The onset degradation temperature for pure PLA was 266°C, which decreased to 255°C for PLA with 5 wt% CNC. This result indicated that the PLA/CNC composites did not undergo significant thermal degradation post-twin-screw blending. Moreover, the onset degradation temperature did not improve with increased CNC content, suggesting poor interfacial adhesion between CNC and the PLA matrix due to CNC aggregation [17].

Differential Scanning Calorimetry (DSC) analysis explored the effects of adding CNC on PLA's crystallization and melting behaviors, with results listed in Table 1. Tg represents the glass transition temperature; Tc is the crystallization temperature during cooling; Tm denotes the melting point; ΔHm represents the melting enthalpy (J/g), calculated by integrating the area under the Tm peak; ΔHc represents the crystallization enthalpy during cooling (J/g), calculated by integrating the area under the Tc peak.

Table 1. Summary of DSC data for pure PLA and PLA/CNC composites

Sample	T_g	T_c	ΔH_c	T_m	ΔH_m	X_c
PLA	59.55	117.58	31.54	149.42	28.78	33.6
1 wt.%CNC	59.62	116.74	29.99	149.65	28.49	32.33
3 wt.%CNC	59.30	118.74	31.02	149.72	30.24	34.13
5 wt.%CNC	59.76	119.06	27.12	149.87	26.81	30.47

Experimental data showed that Tg was unaffected by the incorporation of CNC into PLA and did not change with increasing content, indicating incompatibility between CNC and PLA, with relatively few and large CNCs insufficient to alter the polymer mobility at the glass transition temperature. The adding PEG-graft-CNC increased the crystallinity Xc (%), as CNC served as a nucleating agent promoting crystallization in PLA, provided there was good compatibility and dispersion of CNC within the matrix [16]. A change in Tg was noted due to the addition of PEG-graft-CNC, where PEG's molecular chains, being softer than PLA, facilitated more effortless movement upon heating, thus reducing the overall thermal resistance. In this experiment, an increase in CNC content slightly reduced Xc, likely due to poor dispersion and local aggregation of CNC within the PLA matrix, which inhibited heterogeneous nucleation [18].

Additionally, figure 4b shows the presence of dual melting peaks in the PLA/CNC nanocomposites, attributable to two types of crystalline structures. The lower temperature endothermic peak was due to the melting of PLA crystals. In contrast, the higher temperature peak may have been caused by the reorganization of CNC and the surrounding crystallizable amorphous polymer chains, leading to secondary crystal melting.

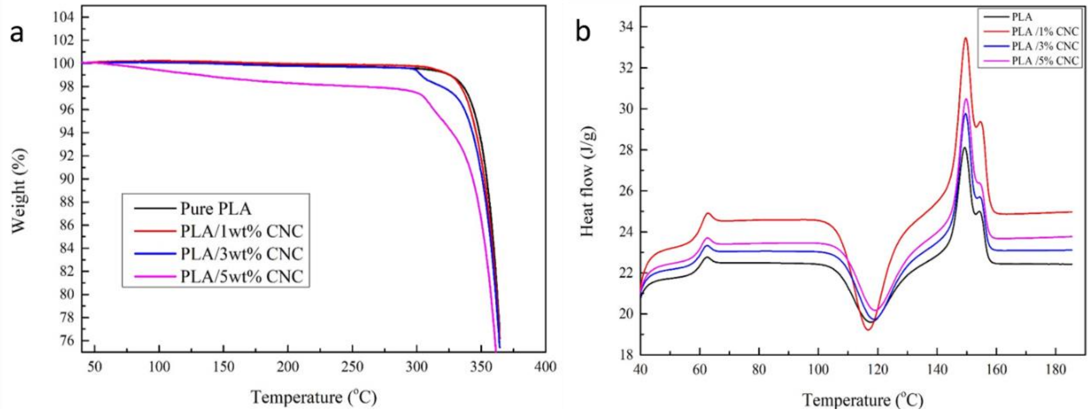

Figure 4. (a) TGA curves (b) DSC thermal analysis for pure PLA and PLA with 1, 3, 5 wt.% CNC

4. Conclusion

The introduction of CNC did not increase the tensile strength of PLA, underscoring the importance of evenly dispersing fillers during the manufacturing process. For PLA/CNC composites to be utilized in the plastic gear industry, addressing the aggregation issue is crucial because their tensile strength is 20.9% lower than the minimum of 10,000 psi (68.94 MPa) recommended by AGMA. The thermal property analysis of the composites showed that secondary aggregation of CNC did not lead to effective crystallization to strengthen the PLA matrix. Additionally, the measured glass transition temperature (T_g) exhibited minimal change, indicating poor interfacial adhesion between CNC and PLA, which led to defects that reduced tensile strength. However, the overall material strengthened, evidenced by an increase in Young's modulus to 3.4 GPa for PLA/5wt% CNC and improved elongation at break for PLA/1wt% CNC.

Future efforts should focus on optimizing the dispersion technique to prevent CNC aggregation, potentially exploring alternative mixing methods or surface modification of CNC. Addressing these issues could lead to substantial improvements in the tensile strength and overall performance of PLA/CNC composites. The refinement of these composites remains promising for developing more sustainable and mechanically robust bioplastics.

Author contribution

Shih-Chen Shi: Conceptualization, Methodology, Resources, Writing- Reviewing and Editing, Supervision, Project administration, Funding acquisition. Chia-Feng Hsieh: Validation, Formal analysis, Investigation, Data Curation, Writing- Original draft. Dieter Rahmadiawan: Writing- Reviewing and Editing

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Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] S.-C. Shi, S.-W. Ouyang, and D. Rahmadiawan, “Erythrosine–Dialdehyde Cellulose Nanocrystal Coatings for Antibacterial Paper Packaging,” *Polymers (Basel)*, vol. 16, no. 7, p. 960, Apr. 2024, https://doi.org/10.3390/polym16070960

[2] S.-C. Shi and J.-Y. Wu, “Deagglomeration and tribological properties of MoS2/hydroxypropyl methylcellulose composite thin film,” *Surf Coat Technol*, vol. 350, pp. 1045–1049, Sep. 2018, https://doi.org/10.1016/j.surfcoat.2018.02.067

[3] S.-C. Shi and T.-F. Huang, “Effects of temperature and humidity on self-healing behaviour of biopolymer hydroxylpropyl methylcellulose for ecotribology,” *Surf Coat Technol*, vol. 350, pp. 997–1002, Sep. 2018, https://doi.org/10.1016/j.surfcoat.2018.03.039

[4] S.-C. Shi, T.-H. Chen, and P. K. Mandal, “Enhancing the Mechanical and Tribological Properties of Cellulose Nanocomposites with Aluminum Nanoadditives,” *Polymers (Basel)*, vol. 12, no. 6, p. 1246, May 2020, https://doi.org/10.3390/polym12061246

[5] D. Rahmadiawan and S.-C. Shi, “Enhanced Stability, Superior Anti-Corrosive, and Tribological Performance of Al2O3 Water-based Nanofluid Lubricants with Tannic Acid and Carboxymethyl Cellulose over SDBS as Surfactant,” *Sci Rep*, vol. 14, no. 1, p. 9217, Apr. 2024, https://doi.org/10.1038/s41598-024-59010-w

[6] S.-C. Shi and Y.-W. Chang, “Biofriendly chitosan-based high-efficiency dialysis membrane,” *Prog Org Coat*, vol. 170, p. 106981, Sep. 2022, https://doi.org/10.1016/j.porgcoat.2022.106981

[7] S.-C. Shi *et al.*, “Rice straw-derived chitosan-enhanced plasticizers as biologically and environmentally friendly alternatives for sustainable materials,” *Int J Biol Macromol*, vol. 264, p. 130547, Apr. 2024, https://doi.org/10.1016/j.ijbiomac.2024.130547

[8] C.-T. Chou, S.-C. Shi, and C.-K. Chen, “Sandwich-Structured, Hydrophobic, Nanocellulose-Reinforced Polyvinyl Alcohol as an Alternative Straw Material,” *Polymers (Basel)*, vol. 13, no. 24, p. 4447, Dec. 2021, https://doi.org/10.3390/polym13244447

[9] D. Rahmadiawan *et al.*, "Tribological Properties of Polyvinyl Alcohol/Uncaria Gambir Extract Composite as Potential Green Protective Film," *Tribology in Industry*, vol. 45, no. 1, pp. 367–274, Jun. 2023, https://doi.org/10.24874/ti.1482.05.23.06

[10] C.-T. Chou, S.-C. Shi, T.-H. Chen, and C.-K. Chen, "Nanocellulose-reinforced, multilayered poly(vinyl alcohol)-based hydrophobic composites as an alternative sealing film," *Sci Prog*, vol. 106, no. 1, p. 003685042311571, Jan. 2023, https://doi.org/10.1177/00368504231157142

[11] S.-C. Shi, X.-N. Tsai, and D. Rahmadiawan, "Enhancing the tribological performance of hydroxypropyl methylcellulose composite coatings through nano-sized metal and oxide additives: A comparative study," *Surf Coat Technol*, vol. 483, p. 130712, May 2024, https://doi.org/10.1016/j.surfcoat.2024.130712

[12] S.-C. Shi and X.-N. Tsai, "Cellulose derivative as protection coating: Effect of nanoparticle additives on load capacity," *Teknomekanik*, vol. 5, no. 2, pp. 90–96, Dec. 2022, https://doi.org/10.24036/teknomekanik.v5i2.16372

[13] Y. Yang, S. Yuan, H. Pan, Z. Li, X. Shen, and Y. Gao, "Catalytically transforming cellulose into methane under natural solar irradiation," *Green Chemistry*, vol. 25, no. 3, pp. 1004–1013, 2023, https://doi.org/10.1039/D2GC04078F

[14] D. Rahmadiawan *et al.*, "Comparative Analysis of the Influence of Different Preparation Methods on the Properties of TEMPO-Oxidized Bacterial Cellulose Powder Films," *Journal of Natural Fibers*, vol. 21, no. 1, Dec. 2024, https://doi.org/10.1080/15440478.2023.2301386

[15] P. Zhang, D. Gao, P. Zou, and B. Wang, "Preparation and thermomechanical properties of nanocrystalline cellulose reinforced poly(lactic acid) nanocomposites," *J Appl Polym Sci*, vol. 134, no. 14, Apr. 2017, https://doi.org/10.1002/app.44683

[16] C. Zhang, M. R. Salick, T. M. Cordie, T. Ellingham, Y. Dan, and L.-S. Turng, "Incorporation of poly(ethylene glycol) grafted cellulose nanocrystals in poly(lactic acid) electrospun nanocomposite fibers as potential scaffolds for bone tissue engineering," *Materials Science and Engineering: C*, vol. 49, pp. 463–471, Apr. 2015, https://doi.org/10.1016/j.msec.2015.01.024

[17] W. Yang *et al.*, "Synergic effect of cellulose and lignin nanostructures in PLA based systems for food antibacterial packaging," *Eur Polym J*, vol. 79, pp. 1–12, Jun. 2016, https://doi.org/10.1016/j.eurpolymj.2016.04.003

[18] L. Wei, U. P. Agarwal, L. Matuana, R. C. Sabo, and N. M. Stark, "Performance of high lignin content cellulose nanocrystals in poly(lactic acid)," *Polymer (Guildf)*, vol. 135, pp. 305–313, Jan. 2018, https://doi.org/10.1016/j.polymer.2017.12.039

[19] S.-C. Shi and X.-A. Chen, "Cellulose circular economy: Amino-functionalized graphene quantum dots as highly sensitive vaccine indicators," *Ind Crops Prod*, vol. 206, p. 117694, Dec. 2023, https://doi.org/10.1016/j.indcrop.2023.117694

[20] I. M. Akbar, A. N. Fauza, Z. Abadi, and D. Rahmadiawan, "Study of the effective fraction of areca nut husk fibre composites based on mechanical properties," *Journal of Engineering Researcher and Lecturer*, vol. 3, no. 1, pp. 19–34, Apr. 2024, https://doi.org/10.58712/jerel.v3i1.126

[21] Z. I. Makruf, W. Afnison, and B. Rahim, "A Study on the utilization of areca nut husk fiber as a natural fibre reinforcement in composite applications: A systematic literature review," *Journal of Engineering Researcher and Lecturer*, vol. 3, no. 1, pp. 18–28, Apr. 2024, https://doi.org/10.58712/jerel.v3i1.123

[22] M. N. Sanad, M. Farouz, and M. M. ElFaham, "Recent advancement in nano cellulose as a biomass-based adsorbent for heavy metal ions removal: A review of a sustainable waste management approach," *Advanced Engineering Letters*, vol. 2, no. 4, pp. 120–142, 2023, https://doi.org/10.46793/adeletters.2023.2.4.1

[23] M. Janmohammadi *et al.*, "Cellulose-based composite scaffolds for bone tissue engineering and localized drug delivery," *Bioact Mater*, vol. 20, pp. 137–163, Feb. 2023, https://doi.org/10.1016/j.bioactmat.2022.05.018

[24] A. Liu *et al.*, "Cellulose nanocrystalline from biomass wastes: An overview of extraction, functionalization and applications in drug delivery," *Int J Biol Macromol*, vol. 241, p. 124557, Jun. 2023, https://doi.org/10.1016/j.ijbiomac.2023.124557

[25] C. M. Agrawal and R. B. Ray, "Biodegradable polymeric scaffolds for musculoskeletal tissue engineering," *J Biomed Mater Res*, vol. 55, no. 2, 2001, https://doi.org/10.1002/1097-4636(200105)55:2<141::AID-JBM1000>3.0.CO;2-J

[26] S. O. Ebhodaghe, "Natural Polymeric Scaffolds for Tissue Engineering Applications," *J Biomater Sci Polym Ed*, vol. 32, no. 16, pp. 2144–2194, Nov. 2021, https://doi.org/10.1080/09205063.2021.1958185

[27] S. Fan *et al.*, "Biomaterial-Based Scaffolds as Antibacterial Suture Materials," *ACS Biomater Sci Eng*, vol. 6, no. 5, pp. 3154–3161, May 2020, https://doi.org/10.1021/acsbiomaterials.0c00104

[28] Y. Kambe, "Functionalization of silk fibroin-based biomaterials for tissue engineering," *Polym J*, vol. 53, no. 12, pp. 1345–1351, Dec. 2021, https://doi.org/10.1038/s41428-021-00536-5

[29] M. A. Naser, A. M. Sayed, W. Abdelmoez, M. T. El-Wakad, and M. S. Abdo, "Biodegradable suture development-based albumin composites for tissue engineering applications," *Sci Rep*, vol. 14, no. 1, p. 7912, Apr. 2024, https://doi.org/10.1038/s41598-024-58194-5

[30] M. Jonoobi, J. Harun, A. P. Mathew, and K. Oksman, "Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion," *Compos Sci Technol*, vol. 70, no. 12, 2010, https://doi.org/10.1016/j.compscitech.2010.07.005

[31] D. Bondeson and K. Oksman, "Dispersion and characteristics of surfactant modified cellulose whiskers nanocomposites," *Compos Interfaces*, vol. 14, no. 7–9, 2007, https://doi.org/10.1163/156855407782106519

[32] E. Fortunati *et al.*, "Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves," *Eur Polym J*, vol. 56, no. 1, 2014, https://doi.org/10.1016/j.eurpolymj.2014.03.030

[33] Y. Peng, Y. Han, and D. J. Gardner, "Spray-drying cellulose nanofibrils: Effect of drying process parameters on particle morphology and size distribution," *Wood and Fiber Science*, vol. 44, no. 4, 2012.

[34] J. Shojaeiarani, D. S. Bajwa, and N. M. Stark, "Spin-coating: A new approach for improving dispersion of cellulose nanocrystals and mechanical properties of poly (lactic acid) composites," *Carbohydr Polym*, vol. 190, 2018, https://doi.org/10.1016/j.carbpol.2018.02.069

[35] N. Herrera, A. P. Mathew, and K. Oksman, "Plasticized polylactic acid/cellulose nanocomposites prepared using melt-extrusion and liquid feeding: Mechanical, thermal and optical properties," *Compos Sci Technol*, vol. 106, 2015, https://doi.org/10.1016/j.compscitech.2014.11.012

[36] J. K. Muiruri, S. Liu, W. S. Teo, J. Kong, and C. He, "Highly Biodegradable and Tough Polylactic Acid–Cellulose Nanocrystal Composite," *ACS Sustain Chem Eng*, vol. 5, no. 5, pp. 3929–3937, May 2017, https://doi.org/10.1021/acssuschemeng.6b03123

[37] L. Quiles-Carrillo, S. Duart, N. Montanes, S. Torres-Giner, and R. Balart, "Enhancement of the mechanical and thermal properties of injection-molded polylactide parts by the addition of acrylated epoxidized soybean oil," *Mater Des*, vol. 140, 2018, https://doi.org/10.1016/j.matdes.2017.11.031