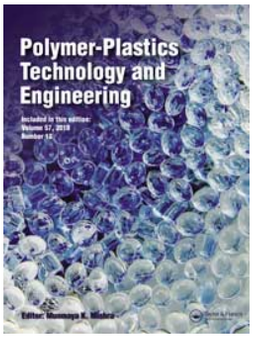

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Facile Preparation of Cellulose/Polylactide Composite Materials with Tunable Mechanical Properties

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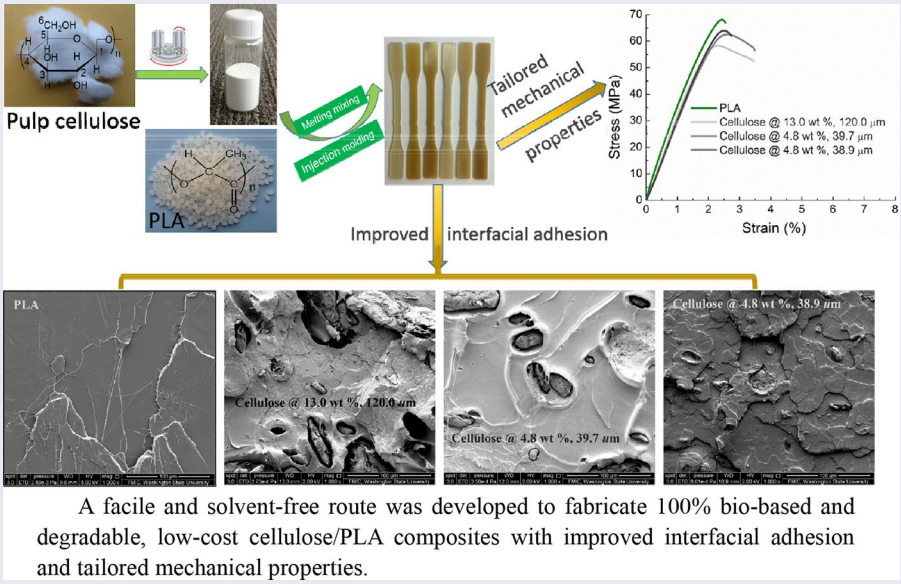
ABSTRACT

A solvent-free route was developed to fabricate 100% biobased, renewable, and degradable polylactide (PLA) composites reinforced with ball-milled celluloses. The results show that the original pulp cellulose fibers were modified to partial amorphization through 30-min ball milling. Filling the ball milled celluloses into PLA increased the tensile modulus for the resultant cellulose/PLA composite materials, while decreased their tensile strength and impact resistance. This method can be used to access the cost-efficient PLA-based composite materials with tunable mechanical properties. The variation analysis shows that filling content contributed more to the variations of their mechanical properties than that particle size did.

KEYWORDS

Ball milling; cellulose; mechanical properties; polylactide; statistical analysis

GRAPHICAL ABSTRACT



A facile and solvent-free route was developed to fabricate 100% bio-based and degradable, low-cost cellulose/PLA composites with improved interfacial adhesion and tailored mechanical properties.

Introduction

Polylactide (PLA) was regarded as the best substitute for various petroleum-based polymers in the framework of environment-friendly processes and products in the past decades, due to its renewability, degradability, biocompatibility, and good thermomechanical properties.[1] Nowadays, however, PLA still suffers from some shortcomings, such as inherent brittleness and relatively high cost for some application scenarios.[2] Adding natural fibers presents a convenient and potential approach to tune, extend, or improve the properties of PLA composites and reduce the cost of products. The effective utilization of raw natural fibers as an indispensable component in polymers for developing novel low-cost eco-friendly composites is one of the most rapidly emerging fields in polymer engineering and science.[3]

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Supplementary data associated with this article can be found through the supplementary content section of this article's web page.

Cellulose is one of the most abundant renewable natural polymers with several well-known advantages, such as low cost, low density, worldwide availability, biodegradability, nontoxicity, high stiffness, and good mechanical properties, which is fibrous and water-insoluble biomaterials in nature. The widespread applications of cellulose reinforcements in environmentally benign polymers have exhibited considerable promise for manufacturing composites with desired properties,[4] such as acceptable specific strength, low density, high toughness, good thermal properties, and complete degradability.[5–7] Natural cellulose fibers have also been used to modify phenolic and epoxy resins.[8] The manufacturing techniques of cellulose composites have been developed, on one hand, from simple casting to more sophisticated methods (i.e., from the most used techniques, such as solution casting, melt-processing of thermoplastic composites, and resin impregnation of cellulose papers using thermoset resins[9] to some recently developed techniques, such as partially dissolved cellulose nanocomposites, nanocomposite foams reinforced with nanocellulose as well as long continuous fibers or filaments), on the other hand, from laboratory to industrially viable methods during the past decades.[10]

Lu et al. reported that incorporation of microcrystalline cellulose (MCC) fibers with different scales into poly(L-lactic acid) (PLLA) increased the stiffness and impact toughness of the resultant composites and improved the crystallization of PLLA.[11] In general, conventional microscale celluloses generally offer limited improvements in physical properties of the resultant composites.[12] In this case, some modification methods, such as surface functionalization[13,14] and graft copolymerization[15] of natural fibers and maleic anhydride grafting to the matrix materials (i.e., PLA),[14] were used to improve their interfacial compatibility, although some previous literature claimed that the interfacial adhesion between PLA and natural fibers is strong.[16] Some bonding agents or binders, for example, ethylene-vinyl acetate copolymer,[17] and some nanoparticles, such as organo-modified montmorillonite[18] and inorganic polysilsesquioxane[19], were used to improve the hybrid cellulose/PLA composites with specific properties such as flame retardation.[19]

Practically, raw pulp cellulose fibers (see the morphology in the upper left of Figure 1) cannot be directly dispersed into polymer matrices uniformly through conventional melting process, due to the large aspect ratio and entangled structures. Chemical modifications to the raw materials (i.e., cellulose and PLA) or its binary blends will usually compromise their degradability and physical properties of the final composite materials or make the fabrication process sophisticated. In this case, some physical pretreatment methods, such as ball milling,[20] pan milling,[21] or shear and cooling milling,[22] were used to destruct their entangled states to improve the mobility and dispersibility in matrix materials and introduce some expected function groups into celluloses, before they are used to fill thermoplastic composites. Among these solvent-free methods, ball milling followed by hot-press molding has been approved a feasible processing methodology to introduce morphology changes and mechanical activation into bacterial celluloses to develop PLA-based composites under dry condition.[23]

There are numerous variables affecting their structures and physical properties for certain materials. Some conceptual frameworks, such as the well-accepted tetrahedron and three-linked chain model,[24] were proposed to help materials scientists and engineers understand the key elements and their interrelationships of materials science and engineering (i.e., processing, structure, properties, and performance). It is favorable for them to design, manufacture, and optimize new materials, if they can easily find the

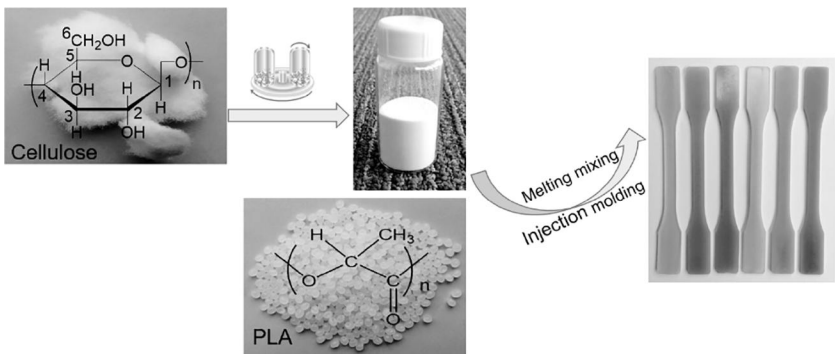

Figure 1. Schematic of fabricating PLA-based composite materials reinforced with the ball-milled celluloses. *Note*: PLA, polylactide.

predominant factor from multivariables after doing some experimental trials as few as possible.

In this context, the aim of this work is to produce 100% biobased, renewable, and degradable cellulose/polymer composites in a solvent-free system. First, pulp cellulose fibers were ball milled to access the suitable filler for the PLA-based composites. Then, the cellulose/PLA composite materials with tunable morphologies and mechanical properties were manufactured through melting extrusion followed by injection molding. The influences of particle size and filling content of the ball-milled celluloses on the structures and mechanical properties of the resultant composite materials were investigated through both experimental and statistical methods from the point of view of structure–property relationships.

Experimental

Raw materials

Pulp cellulose fibers (southern pine, kraft bleached) from Weyerhaeuser Company (Seattle, USA) were stored in a walk-in conditioning room at 20°C and 65% relative humidity, with the initial moisture content of $8.75 \pm 0.22\%$. PLA pellets (3052D) were supplied by NatureWorks LLC (Minnetonka, USA).

Ball milling of cellulose fibers

The cellulose was ground with a planetary ball mill (Across International, PQ-N04) running at 600 rpm for different time. Each of the two 100-ml stainless steel jars was loaded with 3 g of pulp cellulose fibers and 159.20 g of stainless steel balls (100 pieces of Φ6 and 16 pieces of Φ10, respectively).

A laser scattering particle size analyzer (Malvern, Mastersizer 3000) was used to assess particle size and size distribution using distilled water as dispersant. An x-ray diffractometer (Rigaku, MinFlex 600) was used to obtain the diffraction spectra of virgin cellulose fibers and ball-milled particles at the scanning speed of 2°/min and step size of 0.020°. The crystallinity was calculated, according to the peak height method.[25]

Composite fabrication

The schematic of fabricating the binary cellulose-modified PLA-based composite materials is shown in Figure 1. The ball-milled cellulose particles and PLA pellets were dried in a convection oven at 80°C for 24 h prior to extrusion. Then, a series of mixtures of cellulose particles and PLA (weight fractions of cellulose, 4.8, 13.0, and 20 wt%, respectively) were blended with a twin-screw extruder (HAAKE Rheomex CRW 5, MiniLab II) under 75 rpm and 180°C for 5 min.

After cooling with water, the extruded mixtures were chopped with a strand pelletizer (Bay Plastics Machinery, BT25). Then, the pellets were dried in the oven at 80°C overnight prior to injection molding (HAAKE MiniJet). Respectively, the cylinder and mold temperature was 190 and 70°C and the injection and holding pressure was 600 and 400 bar. The injection and holding time was 10 and 30 s, respectively.

Characterization

Mechanical properties

Tensile test with 5 valid replicates was performed under ambient condition, according to ASTM D 638 (Instron 4466). The crosshead speed is 5.08 mm/min. Fracture work of each test bar was calculated by integrating the area under its stress–strain curve.

Morphological properties

Environmental scanning electron microscope (ESEM, Quanta 200, FEI) was used to image the tensile fractured surfaces of the resultant composites after being coated a conducting layer with a gold sputter coater.

Statistical analysis

Analysis of variance (ANOVA; QI Macros, 30-day-trial version) and multiple correlation analysis (SPSS, version 17.0) were conducted to reveal their individual contribution of cellulose particle size and filling content to the morphologies and mechanical properties of the resultant PLA composite materials, respectively.

Results and discussion

Ball milling on the particle characteristics of pulp celluloses

SEM analysis revealed that the original fibrous structure of pulp cellulose almost disappeared after ball milling and was modified to a quasi-circular shape (Figure 2a–c). The morphological destruction of pulp cellulose fibers resulted from the intense impact stress during the ball milling process.[20] The median particle size (i.e., the 50% volume-based diameter, 50% in Figure 2) reached 120 μm for 10 min of ball milling, as shown in Figure 2a,d,e. Longer ball milling time resulted in smaller particle size and narrower size distribution (Figure 2a–e). However, this effect becomes less

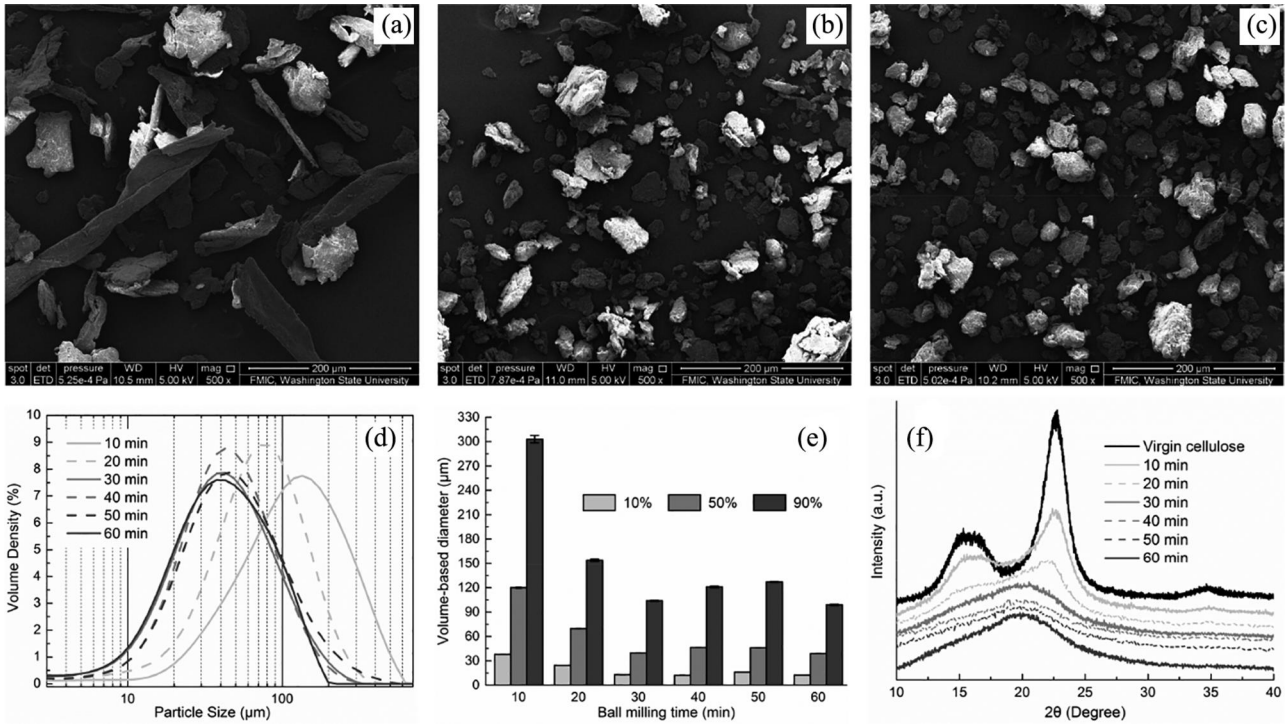

Figure 2. Microscope photographs of the ball-milled cellulose particles (a: 10, b: 30, c: 60 min, respectively), their particle size distributions (d, e), and X-ray patterns (f).

obvious, when ball milling time was over 30 min. For example, the increased ball milling time from 30 to 60 min only leads to a decrease of 0.8 μm in the median particle size (i.e., from 39.7 to 38.9 μm) (Figure 2e).

Howsmon and Marchessault found that ball milling process results in decrystallization of cellulose and the rate of decrystallization can be accelerated by the presence of moisture.[26] According to another previous report by Avolio et al., cellulose shows partial amorphization after 60 min of ball milling, since the crystallinity index of cellulose decreases from 0.53 to 0.15.[20] The crystallinity index of raw pulp cellulose was 0.785, according to Segal's method,[25] while the counterparts with 30 min of ball milling reduced to 0.225. It became partially amorphous when the ball milling time was over 30 min (Figure 2f). The results are consistent with some previous findings.[20,26,27] For the purpose of evaluating particle size on the morphology and mechanical properties of the resultant composites, cellulose particles with the ball milling time of 10, 30, and 60 min were selected as the desired fillers to fabricate PLA composite materials, respectively.

Mechanical properties of the cellulose/PLA composites

Tensile strength and modulus, elongation at break, and fracture work of the virgin PLA and their cellulose-modified composites are illustrated in Figure 3. The tensile strength of cellulose-modified composites is lower than that of virgin PLA, while their tensile modulus is higher than that of PLA. It means that filling the ball-milled cellulose particles into PLA can improve the stiffness of PLA. What is more, data points of the aforementioned mechanical properties for the cellulose-odified PLA-based composites were more concentrated than that of virgin PLA (see error bars in Figure 3). It indicates that modifying PLA with the ball-milled celluloses will improve the processing stability of PLA; furthermore, the products made from these cellulose/PLA composite materials would have more stable quality than that made from virgin PLA.

Both filling content and particle size had some influences on the tensile strength and modulus, elongation at break, and fracture work of the resultant PLA-based composites. For each level of particle size, increasing filling content of the ball-milled cellulose from 4.8 to 20 wt% led to an increase in tensile modulus and a decrease in tensile strength, elongation at break, and fracture work of the resultant composites. At the same level of filling content, the smaller particles led to a decrease in elongation at break and fracture work and an increase in tensile strength, though the trends became less obvious when the filling content increased from 13 to 20 wt%. The tensile modulus distinctly increased with the increase in particle size on the

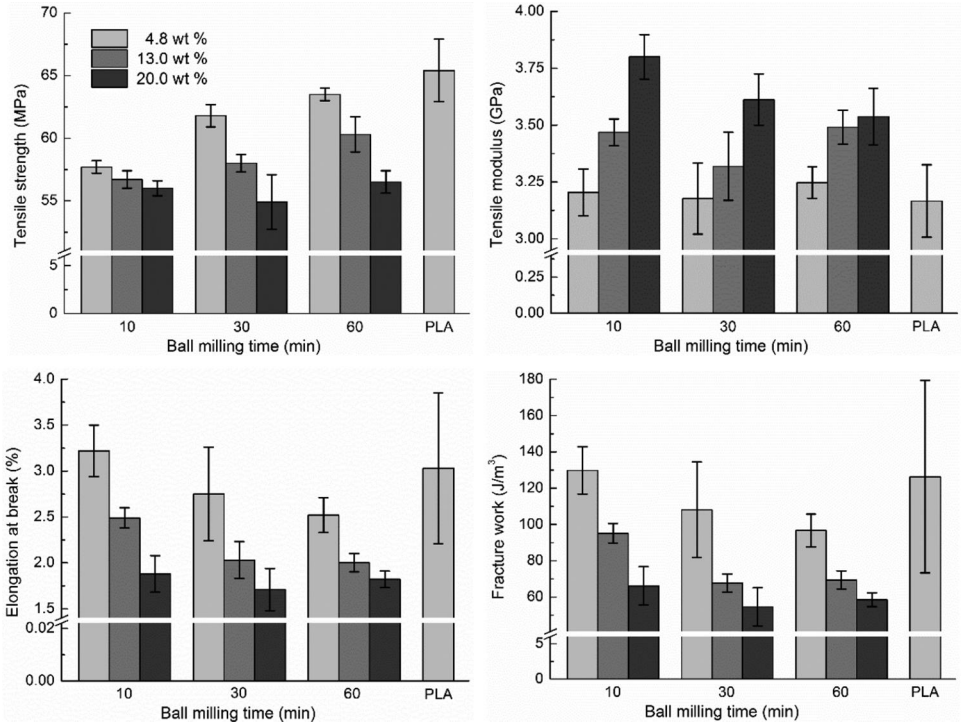

Figure 3. Mechanical properties of the cellulose/PLA composites, with that of PLA as reference. *Note*: PLA, polylactide.

highest level of cellulose content. The results mean that lower filling content and smaller particles of the ball-milled celluloses improved their stress resistance (i.e., tensile strength), while reduced their elastic stiffness (i.e., tensile modulus) of the resultant PLA-based composite materials, due to better wetting and denser compaction of the smaller and less fillers with the PLA matrix.[28] It seems that the cellulose particles with lower filling content and bigger particle size is more likely to improve their plasticity and toughness at the same time than their counterparts do. Ball milling of pulp cellulose fibers under room temperature can be a feasible pretreatment to access the desired fillers to manufacture cellulose/PLA composite materials with tunable mechanical properties.

The mechanical properties of these PLA-based composites can be tailored on the basis of their composition (i.e., particle size and filling content). In another aspect, the variations of the mechanical properties resulting from different particle size and filling content, from the point of view of structure–property relationships, can also be tested through the changes of their fractured morphologies for the resulting composites. As far as the two abovementioned factors are concerned, it looks that filling content played greater effects than particle size, on the variation of the aforementioned mechanical properties, according to Figure 3. This aspect will be further tested through statistical analysis as follows.

Morphologies of the tensile fractured surfaces

As illustrated in Figure 4, the tensile fractured surfaces of the cellulose-modified PLA-based composite materials were totally different from that of PLA, since virgin PLA demonstrated the inherent stiff and brittle fractured surfaces (Supplementary Figure 1).

The fractured surfaces of the PLA composites with larger particles and higher filling content had more microvoids and became rougher and more irregular. These microvoids confirmed the typical pullout pattern of cellulose particles from the matrix PLA during the tensile process. What is more, the interfaces between cellulose particles and PLA became narrower and vaguer for the PLA-based composite materials with lower filling content and smaller particles (Figure 4, from upper right to lower left). Smaller particles and lower filling content of the ball-milled celluloses made better interfacial compatibility, due to the more homogeneous dispersion of cellulose particles in PLA. Thus, better wetting and denser compaction were reached for them. Strong interfacial adhesion results in weak dependence of the extent of reinforcement on the particle characteristics of the reinforcing elements.[16]

Statistical analysis of particle size and filling content on the mechanical properties

Analysis of variation (ANOVA) was used to determine the effects of some variables on the others in the field

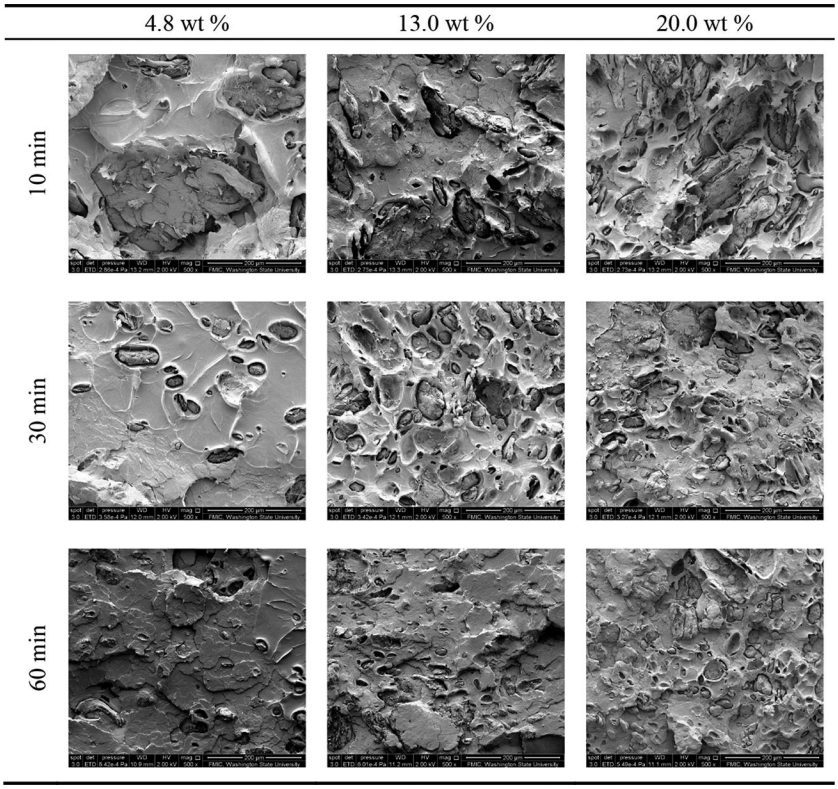

Figure 4. SEM photographs of the tensile fractured surfaces from the cellulose-modified PLA-based composites with different filling contents and particle size. *Note*: PLA, polylactide.

of composite materials.[29] Here, ANOVA with 2 factors and 5 replications was used to the cellulose-modified PLA-based composite materials. As tabulated in Table 1, both particle size and filling content had significant influences on the mechanical properties of resultant composites, since the calculated Fisher values (F in Table 1) are higher than the critical Fisher values (here is 3.259446, since the degree of freedom is 2). This conclusion could also be drawn using p-values, since all the p-values are less than the significance level (i.e., 0.05). The complete ANOVA results can be found in Supplementary Table 1. This means that both filling content and particle size of the ball-milled celluloses had significant influences on the mechanical properties of the resultant PLA-based composite materials through ANOVA.

Pearson correlation has been used to determine the individual effect and direction of some variables on the mechanical properties for composite materials.[30,31] As shown in Table 2, both particle size and filling content of the ball-milled celluloses were negatively related to the tensile strength and positively related to the tensile modulus. However, particle size and filling content were positively and negatively related to the elongation at break and fracture work, respectively. This confirmed the conclusion drawn from Figure 3, since the trends are consistent with each other for most of the abovementioned scenarios.

The correlation coefficients between the filling content and their mechanical properties are higher (the minimum absolute value, 0.734) than the

Table 1. Results of ANOVA.

Factor	Mechanical property	F	p value
Particle size	Tensile strength*	86.10019	0.000
	Tensile modulus*	60.13363	0.000
	Elongation at break*	67.36008	0.000
	Fracture work*	74.44415	0.000
Filling content	Tensile strength*	35.59468	0.000
	Tensile modulus*	4.589986	0.017
	Elongation at break*	12.88337	0.000
	Fracture work*	16.14727	0.000

*Means significant at the 0.05 level (2-tailed).

Table 2. Results of Pearson correlation.

Factor	Mechanical property	Pearson coefficients	Significance
Particle size	Tensile strength	−0.391**	0.008
	Tensile modulus	0.200	0.188
	Elongation at break	0.352*	0.018
	Fracture work	0.378*	0.010
Filling content	Tensile strength	−0.734**	0.000
	Tensile modulus	0.817**	0.000
	Elongation at break	−0.804**	0.000
	Fracture work	−0.807**	0.000

*,**Means significant at the 0.05 and 0.01 level (2-tailed), respectively.

counterparts between particle size and mechanical properties (the maximum absolute value, 0.391). The statistical results showed that filling content contributes more to the variations of the mechanical properties than particle size does, which confirms the preliminary conclusion drawn from the experimental measurement (Figure 3). Statistical methods combining with experimental trials can be used to determine the predominant one from multivariables easily.

Conclusion

This work demonstrated a green and efficient route to manufacture 100% biobased, renewable, and degradable composite materials with tailored mechanical properties and structures. Ball milling was used to physically pretreat pulp cellulose fibers to access the desired fillers. Then, the PLA-based composite materials were fabricated through extrusion blending followed by injection molding. Their physical properties and structures were investigated through experimental tests and statistical analysis.

The results show that the original fibrous structure of pulp cellulose fibers disappeared and was modified to the quasi-circular shape after ball milling. Longer ball milling of the pulp cellulose fibers resulted in smaller particle size, narrower size distribution, and lower crystallinity. The cellulose particles that experienced ball milling more than 30 min demonstrated the partial amorphization by XRD analysis. Smaller particles and lower filling content of the ball-milled celluloses led to more homogeneous dispersion in PLA. Particle size and filling content of the ball-milled celluloses influenced not only on the morphologies of the fractured surfaces but also significantly on the tensile strength and modulus, elongation at break, and fracture work of the resultant composite materials. Filling the ball-milled celluloses into PLA improved its tensile modulus and the stabilities of their mechanical properties for the resultant cellulose/PLA composite materials, which will endow them with tunable mechanical properties for different application scenarios. The ball-milled celluloses with lower filling content and bigger particle size are more likely to improve their plasticity and toughness at the same time than their counterparts do.

The filling content contributed more to the variations of their mechanical properties, compared with that the particle size did. Statistical analysis of experimental data can be used to effectively estimate the effects of multivariables on the physical properties of the resultant composites and identify the predominant one, which will accelerate the design, manufacture, and optimization of some advanced materials in future.

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