Research Article

Preparation and Supercritical CO$_2$ Foaming of Modified Nanocrystalline Cellulose Reinforced Polylactic Acid Bionanocomposites

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The solution casting method was used to prepare polylactic acid/modified nanocrystalline cellulose (PLA/mNCC) composites, and the effects of the mNCC content on the morphology, thermal characteristics, and rheological properties of the PLA nanocomposite were examined. The PLA microcellular foaming nanocomposite was prepared using supercritical CO$_2$ foaming. Furthermore, the foaming conditions were optimized, and the effect of NCC surface modification, as well as the content and interfacial force of nanoparticles, on the foaming efficiency and cell pattern of composites was examined. The results suggested that a sufficient number of nanoparticles increased the nucleation site for foaming and played a vital role in heterogeneous nucleation in the foaming system. An ideal microcellular foaming material with an average cell diameter of 6.97 μm and a cell density of 6.05 × 10$^9$ cells/cm$^3$ was prepared when the foaming temperature was 110°C, the foaming pressure was 18 MPa, the incubation period was 2 h, and the mNCC content was 6%.

1. Introduction

Microcellular foaming plastics exhibit a wide range of excellent properties, including lightweight, strong moisture absorption, high impact strength, good thermal insulation and sound insulation, and high specific strength. Thus, microcellular foaming plastics are suitable for a variety of applications, including cushion packaging, food packaging, structural materials, and sound insulation [1–3]. Polystyrene (PS), polyurethane (PU), polyvinyl chloride (PVC), and poly(methyl methacrylate) (PMMA) foams are the most prevalent polymer foam materials nowadays. The achievement of biodegradability and recycling of these systems remains a significant challenge. Additionally, the inevitable depletion of fossil fuels and growing environmental concerns encourage researchers to develop biodegradable polymer foams to replace the petroleum-based materials currently employed [4–7].

Polylactic acid (PLA) is a thermoplastic polymer made from the renewable agricultural raw material corn. It is well-known for its renewability, biodegradability, high mechanical strength, thermoplastic properties, and low cost [8–10]. It has a wide range of uses in a variety of fields, most notably in the packaging and biomedical sectors [11–14]. PLA has also been employed to develop foaming materials with microcellular structures. PLA, on the other hand, has low melt strength, a restricted processing window, a low foaming rate, and a poor cell pattern, all of which make it difficult to produce [15]. Several previous studies have demonstrated that adding nanoparticles (e.g., cellulose nanocrystals, clay, talc, or silica) significantly improves the foaming efficiency of PLA [16–18]. The nanoparticles not only improve the melt strength of the material but also play the role of heterogeneous nucleation during the foaming process. Lin et al. [19] prepared PLA/NCC/PEG microcellular foam material using nanocrystalline cellulose (NCC) as a nucleating agent. The findings demonstrated
that NCC acted as a heterogeneous nucleation agent during the foaming process. The volume expansion rate of foam increased as the NCC concentration increased, whereas cell diameter decreased and cell density increased. Ameli et al. [20] found that nanoclay improved the crystallinity and melt strength of PLA, significantly improved its foaming behavior, and promoted the refinement and uniform distribution of cells. Wang et al. [21] prepared PLA/graphite foam-up nanocomposite with a density of 0.7 g/cm$^3$ and a uniform microporous structure by using nanographite to facilitate the crystallization of PLA and increase its viscoelasticity.

NCC is an organic nanoparticle that is naturally occurring and sustainable. It has a large specific length and diameter as well as a high strength. NCC modification not only can increase the melt strength of PLA but also can improve foaming performance and broaden its application range. Additionally, both PLA and NCC are formed from biomass and can be biodegraded following their use [22–24]. However, due to the high hydrophilicity of the NCC polyhydroxyl groups, they readily agglomerate in the PLA matrix, and hence the surface hydrophobic modification of NCC was typically performed [25]. Modification techniques that were often utilized included physical adsorption modification [26–29], esterification modification properties [30–33], graft copolymerization [34–37], and silane coupling agent modification [38–41]. The modified NCC could be more uniformly dispersed in the polymer matrix and played an effective role as nanoparticles.

Kasa et al. [42] and Ali et al. [43] used solution casting to successfully prepare acetylation-modified NCC and PLA nanocomposites. Acetylated NCC exhibits increased dispersion in polymer matrixes, indicating that the acetylation reaction enhanced NCC’s capability to be used as a reinforcing material in PLA. Jiang et al. [44] used cetyltrimethyl ammonium bromide-modified NCC and found that the surface modification of NCC improved the dispersion state of NCC in the natural rubber matrix as well as the interfacial interaction between natural rubber and NCC.

The purpose of this study was to produce a completely biodegradable PLA microcellular foaming nanocomposite. First, the hydrophobicity of nanocrystalline cellulose was increased by acetylation, and then a solution casting approach was used to produce a polyactic acid/modified nanocrystalline cellulose (PLA/mNCC) nanocomposite. Investigations were carried out on the effects of mNCC at various concentrations on the morphology, thermal characteristics, and rheological properties of a PLA nanocomposite. Finally, the foaming of PLA nanocomposite was studied using supercritical CO$_2$ foaming. The foaming process parameters including temperature, pressure, and time were optimized, and the effects of surface modification of NCC, nanoparticle content, and interfacial force on the foaming performance and cell pattern of composites were explored.

2. Experimental

2.1. Materials. Polylactic acid (PLA), 2003D, with a molecular weight (Mn) of ca. 2.15 × 10$^4$ g mol$^{-1}$ (determined using an Ubbelohde viscosity meter at 25°C with chloroform as the solvent), was acquired in pellet form from Natureworks Co. PLA pellets were dried in a vacuum oven at 70°C for 12 h. NCC was supplied by the Beijing Nanocrystalline Cellulose Technology Research and Development Centre of China International Tourism and Trade Co. Ltd. (China). NCC had a diameter of 20–50 nm and a length of 200–500 nm. Ningbo Fangxin Co. Ltd. (China) provided CO$_2$ with a purity of 99%. Sinopharm Chemical Reagent Co. Ltd. (China) provided the acetic acid, perchloric acid, acetic anhydride, ethyl alcohol, and dichloromethane used in this study. No additional purification was performed on any reagents.

2.2. Methods

2.2.1. Modification of NCC by Acetylation. Acetic acid, perchloric acid, and acetic anhydride (1 g of NCC to 25 mL of toluene, 20 mL of acetic acid, 0.1 mL of perchloric acid, and 7 mL of acetic anhydride) were added to the tolune ultrasonic solution of NCC and stirred at room temperature for 1 h. The mixture was then poured into ethanol to precipitate a white flocculent precipitate that was centrifuged and washed three times with ethanol and deionized water to yield an acetic anhydride-modified NCC aqueous solution. The mixture was then freeze-dried to a constant weight to yield a white solid powder, which was named acetic anhydride-modified NCC (mNCC) [45].

2.2.2. Preparation of PLA Nanocomposite. The solvent casting approach was used to prepare PLA/mNCC nanocomposites [46]. The resultant mNCC aqueous solution was replaced with a solution to produce mNCC CH$_2$Cl$_2$ solution, which was ultrasonically dispersed in an ice-water bath. After that, a certain amount of PLA was dissolved in a 10% mNCC CH$_2$Cl$_2$ solution at 40°C. After the mixture had been well mixed, it was ultrasonically dispersed and then placed in a vacuum oven for 1 h before being cast on the film. The mixture was vacuum dried before being hot-pressed into a sheet to produce composites with mNCC concentrations of 0%, 2%, 4%, 6%, and 8%, indicated as PLA, PLA/mNCC-2, PLA/mNCC-4, PLA/mNCC-6, and PLA/mNCC-8, respectively.

2.2.3. Supercritical CO$_2$ Foamed PLA Nanocomposite. The PLA nanocomposite sample was placed in the foaming chamber. The switch was tightened after the air in the chamber had been removed. CO$_2$ was continuously injected into the chamber to adjust the pressure, causing the CO$_2$ to reach a supercritical state. The temperature was maintained, and the material was soaked in supercritical CO$_2$ for a certain time. Then, the pressure was quickly released, and the material was placed in an ice-water bath to cool and shape to obtain a PLA microcellular foaming nanocomposite as shown in Figure 1.

2.3. Characterization

2.3.1. Characterization of the Cross-Sectional Morphology of a PLA Nanocomposite. Field emission scanning electron microscopy (FE-SEM; S-4800, Hitachi, Japan) was used to
examine the cross-sectional morphology of a PLA nanocomposite. The samples were quenched and brittle cracked in liquid nitrogen before being sprayed with gold (platinum) and examined using an FE-SEM.

2.3.2. Thermal Stability Analysis of PLA Nanocomposite. The thermal stability of PLA nanocomposite was analyzed using a thermogravimetric analyzer (TGA; SDT Q600, TA Corporation, USA). In a nitrogen atmosphere, 1 mg of PLA nanocomposite was subjected to thermogravimetric analysis. The gas flow rate was set to 20 mL/min; the temperature range was set to room to 600°C; and the heating rate was set to 10 °C/min.

2.3.3. Dynamic Thermomechanical Analysis of PLA Nanocomposite. The dynamic thermomechanical analysis (DMA) of PLA nanocomposite was performed using a dynamic thermomechanical analyzer (Q800, TA, USA) operating at a frequency of 10 Hz, a temperature range of −50 to 100°C, and a heating rate of 3°C/min. The experimental sample had a dimension of 30 mm × 5 mm and a thickness of 1 mm.

2.3.4. Analysis of the Rheological Properties of a PLA Nanocomposite. A rotational rheometer (Physica MCR301, Anton Paar, Austria) was used to determine the rheological properties of a PLA nanocomposite. The sample was a disc with a thickness of 1 mm and a diameter of 25 mm. The temperature throughout the test was 170°C, and the frequency ranged from 0.01 to 100 Hz. The sample must be dried prior to the test.

2.3.5. Characterization of PLA Microcellular Foaming Nanocomposite Sections Using Scanning Electron Microscopy. The microstructure of the PLA microcellular foaming nanocomposite cell was characterized by scanning electron microscopy (SEM; TM1000, Hitachi, Japan). The foaming material samples were quenched and brittle cracked with liquid nitrogen, then sprayed with gold (platinum), and examined under SEM.

2.3.6. Cell Diameter of PLA Microcellular Foaming Nanocomposite. The cell diameter of the PLA microcellular foaming nanocomposite was statistically examined using the particle size distribution calculating software Nano Measurer. The SEM images of the cells were counted multiple times, and the average value was taken to ensure the accuracy of the statistics.

2.3.7. Density of PLA Microcellular Foaming Nanocomposite. The density of PLA microcellular foaming nanocomposite was assessed using the capillary pycnometer method [47], which used the density of water to calculate the buoyancy method. Following (1), the density of foaming material samples was estimated. Each group of samples was measured three times, and the findings were calculated based on the average of the three measurements.

\[
\rho_{\text{foam}} = \frac{m \rho_{\text{water}}}{m + m_1 - m_2} \tag{1}
\]

where \( \rho_{\text{foam}} \) is the sample density, \( g/cm^3 \); \( \rho_{\text{water}} \) is the water density (obtained by the mass-to-volume ratio of water in the pycnometer), \( g/cm^3 \); \( m \) is the mass of the sample; \( m_1 \) is the mass of the water after filling the pycnometer; and \( m_2 \) is the mass of the pycnometer containing the water and the sample.

2.3.8. Volume Expansion Rate of PLA Microcellular Foaming Nanocomposite. The volume expansion rate of a PLA microcellular foaming nanocomposite can be calculated using the following formula:

\[
V_f = \frac{V_{\text{foam}}}{V} = \frac{m \rho_{\text{foam}}}{m / \rho} = \frac{\rho}{\rho_{\text{foam}}} \tag{2}
\]

where \( V_f \) is the volume expansion rate of the sample, that is, the foaming ratio, in \( cm^3 \); \( V_{\text{foam}} \) and \( V \) are the volumes of foamed and nonfoamed materials, in \( cm^3 \), respectively; and \( \rho_{\text{foam}} \) and \( \rho \) are densities of foamed and nonfoamed materials, in \( g/cm^3 \), respectively.

**Figure 1:** Supercritical CO₂ foaming process.
2.3.9. **Cell Density of PLA Microcellular Foaming Nanocomposite.** The cell density of PLA microcellular foaming nanocomposite is commonly represented in terms of the number of cells per unit volume, and the formula for calculating it is shown in the following equation [48, 49]:

\[ N = \left( \frac{n}{A} \right)^{3/2} \times V_f, \]  

where \( N \) is the cell density of the foaming material, in cells/cm\(^3\); \( A \) is the area of the area used for analysis in the SEM image, in cm\(^2\); \( n \) is the number of cells in the area used for analysis in the SEM image; and \( V_f \) is the volume expansion rate of the foaming material, that is, the foaming ratio, in cm\(^3\).

3. **Results and Discussion**

3.1. **Morphology of PLA Nanocomposite.** FE-SEM was used to investigate the PLA nanocomposite’s cross-sectional morphology. The cross-sectional morphology of mNCC composites with varying contents is shown in Figure 2. The section of pure PLA is smooth and flat, as illustrated in Figure 2, which is distinct from that of other composites. Although the mNCC was equally dispersed throughout the PLA matrix, as the mNCC content increased, a small amount of agglomeration formed as a result of the hydrogen bonding interaction between the unmodified hydroxyl groups on the surface of the NCC [50].

3.2. **Thermal Stability Analysis of PLA Nanocomposite.** The TGA technique was employed to investigate the thermal degradation of the PLA nanocomposites. According to the TG and DTG curves in Figure 3, the neat PLA and PLA nanocomposites began to lose weight when exposed to temperatures between 300 and 400°C. The onset weight loss temperature of the nanocomposites continued to decrease with the addition of the mNCC. The nanocomposite’s lower thermal degradation performance was mostly related to the NCC’s low thermal stability [51, 52]. While the PLA nanocomposites demonstrated a lower thermal decomposition capability than pure PLA, their initial weight loss temperature remained above 300°C, which meets the requirements for a wide variety of applications.

3.3. **Dynamic Thermomechanical Analysis of PLA Nanocomposite.** Figure 4 illustrates the storage modulus \( E' \) and loss factor tan\( \delta \) curves of PLA and its nanocomposites as a function of temperature. As shown in Figure 4(a), when the temperature was lower than 45°C, the increase in storage modulus \( E' \) with mNCC concentration could be attributed to the formation of cross-linked structures, an increase in crystallinity (more ordered regions developed), and better mNCC dispersion in the PLA matrix, which resulted in improved mNCC adhesion [48]. The storage modulus \( E' \) of PLA and its nanocomposites reduced dramatically with increasing temperature between 45°C and 70°C because of the glass transition.

The effect of mNCC content on the loss factor of PLA nanocomposite is shown in Figure 4(b). As observed, the loss factor (tan\( \delta \)) in the PLA nanocomposites’ glass transition region reduced as mNCC concentration increased, and the nanocomposites’ loss factor (tan\( \delta \)) was significantly less than that of pure PLA. Pure PLA contained a single transition peak, but as mNCC was added, more prominent double peaks appeared gradually, demonstrating that mNCC can cause crystallization of PLA [52]. Furthermore, changes in mNCC content had a negligible effect on the glass transition temperature of PLA nanocomposite [53].

3.4. **Analysis of the Rheological Properties of a PLA Nanocomposite.** We investigated the dynamic rheological properties of PLA nanocomposites. At 170°C, Figure 5 illustrates the frequency dependence of the storage modulus \( G' \), the loss modulus \( G'' \) and the complex viscosity \( \eta^* \) of the PLA/mNCC nanocomposites. As found, when the mNCC content was increased, both the storage modulus and the loss modulus increased, with the storage modulus approaching the loss modulus in the low-frequency region, suggesting that the PLA/mNCC nanocomposite had become more viscoelastic as the mNCC content was increased [54].

Furthermore, the \( \eta^* \) in the low-frequency region of PLA remained relatively constant as the scanning frequency \( \omega \) was increased, similar to a Newtonian fluid, whereas the PLA/mNCC composites exhibited relatively clear shear-thinning behavior. The complex viscosities of the PLA/mNCC nanocomposites were found to be greater than those of pure PLA and increased as the mNCC content increased. The high viscosities of the polymer matrix with nanometric cellulose fillers were attributed to filler-filler interactions via hydrogen bonding as well as an excellent filler-matrix interfacial interaction. As a result, the flow restrictions of the PLA chains were caused by the strong interaction between the mNCC and the PLA molecules, which increased the melt viscosity of the PLA/mNCC nanocomposites [55]. However, the complex viscosity of the PLA/mNCC-8 nanocomposite did not increase considerably, which could be attributed to the agglomeration of the high content nanofiller. These findings are in accordance with the SEM micrographs.

3.5. **Effect of Foaming Process Conditions on Composites Cell Pattern.** The effects of foaming processing parameters such as foaming temperature, foaming pressure, and incubation time on the cell pattern of composites were explored using PLA/mNCC-6 composites as the research object.

Figure 6 illustrates cross-sectional SEM images of the foamed PLA/mNCC foaming material after a 2 h incubation period and a foaming pressure of 16 MPa at various foaming temperatures. It was found that the foaming material produced by composites at a foaming temperature of 110°C had the most homogeneous cells, the smallest size, and the most complete shape in the range of 90–150°C. Figure 7 shows the influence of various foaming temperatures on the average cell diameter and density of the foaming material, as well as...
Figure 2: FE-SEM micrographs of the PLA nanocomposites: (a) pure PLA, (b) PLA/mNCC-2, (c) PLA/mNCC-4, (d) PLA/mNCC-6, and (e) PLA/mNCC-8.

Figure 3: Thermal decomposition of the pure PLA and PLA nanocomposites at a heating rate of 10°C min⁻¹ under nitrogen.

Figure 4: Dynamic thermomechanical analysis of PLA and its nanocomposites: (a) storage modulus and (b) loss factor.
the foam density and volume expansion rate. It was observed that the cell density was greatest at a foaming temperature of 110°C.

The foaming temperature had a considerable effect on the cell pattern of the composites, as demonstrated. It was observed that when the foaming temperature was lower, the diffusion rate of CO₂ in the polymer matrix was slow. As a result, the dissolution equilibrium could not be reached, and the distribution was not uniform, resulting in partial material foaming. CO₂ slowly diffused into the polymer matrix and reached dissolution equilibrium as the temperature increased, resulting in the completion of the foaming process, which gradually improved the cell structure. Increasing the temperature resulted in a decrease in melt strength and a decrease in surface tension, which caused the cells to squeeze one another, causing the cells to grow larger, merge, and rupture. In addition, the size of the cells became irregular, and the density of the cells also decreased. Rapid depressurization and cooling molding allowed the comparatively low foaming temperature of 110°C to be rapidly decreased to below the system’s glass transition temperature $T_g$ in a short time, resulting in a relatively short cell growth time and a small and even cell size.

Figure 8 illustrates cross-sectional SEM images of the foamed PLA/mNCC foaming material at a temperature of 110°C and incubation period of 2 h under the influence of various foaming pressures. Figure 9 shows a trend diagram showing the effect of varying foaming pressures on the average cell diameter and density of the foaming material, as well as the density of the foam and the rate of volume expansion. When the foaming pressure was low, it was noticed that the CO₂ did not reach dissolution equilibrium in the polymer matrix, then the number of nucleation was low, and an unfoamed area appeared in the composites. The cell pattern was poor, and the size was not uniform. The solubility of CO₂ in the polymer matrix increased progressively as the foaming pressure increased, as was the rate of bubble nucleation; the cell diameter of the foaming material dropped; and the cell size distribution became more uniform. Meanwhile, after saturation of the matrix with high-pressure CO₂, the molecular chain movement was accelerated; the viscosity of the composite melt lowered; the nucleation and growth resistance

![Graphs](image-url)
of cells were decreased; and the cell structure was enhanced. Therefore, when the foaming pressure was 18 MPa in the 12–18 MPa research range, the cell size was reduced, and the cell structure was relatively excellent.

Figure 10 depicts cross-sectional SEM images of foamed PLA/mNCC foaming material with a foaming temperature of 110°C and a foaming pressure of 16 MPa at various incubation times. Figure 11 depicts a trend diagram illustrating the effect of various incubation times on the average cell diameter and density of the foaming material, as well as the foam density and volume expansion rate. It was found that after approximately 2 h of incubation, the dissolved CO2 in the polymer matrix achieved saturation and that further extension of the incubation time had minimal influence on the cell structure.

3.6. Influence of NCC Surface Modification on Composites Cell Pattern. The cell pattern, diameter, and density of PLA/mNCC and PLA/NCC microcellular foaming nanocomposite
were compared in Figures 12 and 13 under the same foaming conditions (110°C, 18 MPa, 2 h). It was found that when nanoparticles were added at a concentration of 2% and 6%, the average cell diameter of the PLA/mNCC microcellular foaming nanocomposite was significantly smaller, the average cell density was considerably greater, and the cell pattern was markedly better than that of the PLA/NCC microcellular foaming nanocomposite. This was primarily owing to the difference in dispersion state and interaction of the nanofillers with the PLA matrix generated by the different surface characteristics of NCC and mNCC. Nanoparticle aggregation or their strong interaction with the PLA matrix typically lowers their nucleation effectiveness. More nucleation sites can be provided by enhanced nanoparticle dispersion, which necessitates improved phase adhesion. Improved polymer-particle compatibility, on the other hand, is deleterious to nucleation since weak phase interfaces are typically favored for heterogeneous nucleation during physical foaming. Acetylation may increase the interfacial interaction between PLA and NCC particles, resulting in a more uniform distribution of mNCC in PLA than in NCC. The decreased aggregation and increased effective filling of the filler particles

Figure 8: Cell structure of foaming material under different foaming pressure (2 h, 110°C): (a) foaming pressure 12 MPa, (b) foaming pressure 14 MPa, (c) foaming pressure 16 MPa, and (d) foaming pressure 18 MPa.

Figure 9: Effect of different foaming pressure on foaming of composites (2 h, 110°C).
indicate that the PLA/mNCC contained more additional nucleation sites. This may compensate for the loss in nucleation capacity of each NCC particle induced by surface acetylation, resulting in increased nucleation efficiency of the PLA/mNCC nanocomposites [17, 56].

3.7. Influence of Content and Interfacial Force of mNCC on Composites Cell Pattern. The pure PLA and PLA/mNCC composites were microcellular foamed using supercritical CO₂ at 110°C for 2 h, and the cross-sectional structure and cell pattern of the microcellular foam material were studied using SEM, as shown in Figure 14. The average cell diameter and density of foaming material were analyzed and compared in Figure 15. It was discovered that the PLA/mNCC foaming nanocomposite had a significantly improved cell pattern compared to pure PLA. When the nanoparticle concentration was less than 6%, increasing the mNCC content resulted in a decrease in the average cell diameter of the foaming material and a more homogeneous size distribution. Furthermore, the cell pattern was improved; the wall thickness was enhanced; and the cell structure was optimized. This was because mNCC acted as a heterogeneous nucleating agent in the compound foaming system. During the foaming process, the free energy barrier to be overcome in heterogeneous nucleation was lower than that in homogeneous nucleation; cell nucleation was easier; and the number of nucleation sites in heterogeneous nucleation was determined by the number of nucleation attachment points in the composite [49]. Therefore, as the mNCC

![Figure 10: Cell structure of foaming material under different incubation times (110°C, 16 MPa): (a) foaming time 0.5 h, (b) foaming time 1 h, (c) foaming time 2 h, (d) foaming time 4 h, and (e) foaming time 8 h.](image)

![Figure 11: Effects of different incubation times on foaming of composites (110°C, 16 MPa).](image)
content increased, the number of nucleation sites increased, and the cell density increased accordingly. However, when the mNCC content was increased to 8%, neither the average cell diameter nor the cell density rose considerably, indicating that the cell structure remained comparable to that of the 6% content. This was mostly due to the high mNCC content, which resulted in an increase in the number of unreacted hydroxyl groups on the surface, which led to a little agglomeration, resulting in mNCC clusters distributed throughout the PLA matrix. Since the number of nucleation sites was lowered in comparison to single mNCC, there was no substantial increase in nucleation sites.

To conduct a more detailed examination of the effect of mNCC on the foaming process of composites, the interfacial at the nucleation site was determined as a force [57]:

$$N = C_f \exp \left[ \frac{-16\pi r^3}{3(\Delta P)k_B T} \right] = \log N$$

$$= \frac{16\pi}{3k_B T} \times \frac{r^3}{(\Delta P)^2} + \log C_f,$$

where $N$ is the cell density, in cell/cm$^3$; $C$ is the concentration of CO$_2$ and/or the concentration of heterogeneous nanocellulose content (%)

![Figure 12: Comparative analysis of PLA foaming nanocomposite cell structures (110°C, 18 MPa, 2 h): (a) PLA/NCC-2, (b) PLA/NCC-6, (c) PLA/mNCC-2, and (d) PLA/mNCC-6.](image)

![Figure 13: Average cell diameter and cell density (110°C, 18 MPa, 2 h of PLA foaming nanocomposite).](image)
nucleation sites; \( f \) denotes the collision frequency of \( \text{CO}_2 \); \( r \) denotes the interfacial tension, in \( \text{mJ/m}^2 \); \( \Delta P \) is the foaming pressure, MPa; \( k_B \) is Boltzmann constant, \( \text{J/K} \); and \( T \) is the absolute foaming temperature, K.

The logarithm of the cell density was supposed to be linear with the parameter \( \Delta P^2 \) in classical nucleation theory. As indicated in formula (4), the nucleation site’s interfacial force can be determined using the slope of the regression line. The regression line’s vertical shift was associated with the number of nucleation sites or the concentration of \( \text{CO}_2 \) molecules and may have been influenced by cell merger, which was not incorporated in the equation.

The slopes of the regression line for pure PLA and pure PLA nanocomposite are listed in Figure 16. The interfacial force of each material nucleation site is calculated using the slope and formula as follows: 3.59 mJ/m² for pure PLA, 2.96 mJ/m² for PLA/mNCC-2, 2.62 mJ/m² for PLA/mNCC-4, 2.81 mJ/m² for PLA/mNCC-6, and 2.88 mJ/m² for PLA/mNCC-8. As can be observed, the interfacial force between the PLA nanocomposite and pure PLA was significantly less than that of pure PLA at the nucleation site. The addition of mNCC decreased the nucleation site’s interfacial force and increased nucleation efficiency, owing to the greater interaction between the carboxyl groups and \( \text{CO}_2 \) produced on

![Figure 14: Cell structures of different pressures and different nanoparticle content foaming nanocomposite (110°C, 2 h).](image-url)
the surface of the mNCC. However, as the mNCC concentration increased, agglomeration occurred; the nucleation site decreased; the interfacial force remained constant; and the nucleation efficiency remained constant.

4. Conclusions

The solution casting approach was used to successfully prepare a PLA/mNCC nanocomposite. However, when the mNCC content increased, the agglomeration phenomenon became more evident. The addition of mNCC did not affect the thermal weight loss of composites and had a negligible effect on the glass transition temperature Tg of the material, as determined by thermal analysis, dynamic thermomechanical analysis, and rheological test. The storage modulus $G'$, loss modulus $G''$, and complex viscosity $\eta^*$ of composites increased as the mNCC content increased, and the storage modulus increased more dramatically, approaching the loss modulus in the low-frequency region, indicating that mNCC restricted the motion of the PLA macromolecular chain and significantly improved the melt viscoelasticity of composites.

The foaming process parameters such as temperature, pressure, and time were optimized using supercritical CO2 foamed PLA and its nanocomposites, and the effects of surface modification of NCC and mNCC content on the foaming performance and cell pattern of composites were compared. The addition of an appropriate amount of mNCC increased the nucleation site for foaming and acted as a heterogeneous nucleation agent in the foaming system. In the aforementioned research range, the average cell diameter was 6.97 $\mu$m, and the cell density reached $6.05 \times 10^9$ cells/cm$^3$ under the conditions of a foaming temperature of 110°C, foaming pressure of 18 MPa, incubation period of 2 h, and mNCC content of 6%, indicating that the material was an ideal microcellular foaming material.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no known conflicts of interest or personal relationships that could have appeared to influence the work reported in this paper.

Authors’ Contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.
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References

[1] A. Jennifer, J. Villamil, N. Le Moigne et al., “Foaming of PLA composites by supercritical fluid-assisted processes: a review,” *Molecules*, vol. 25, no. 15, p. 3408, 2020.

[2] S. Standau, C. Zhao, S. Murillo Castellón, C. Bonten, and V. Altstädt, “Chemical modification and foam processing of polylactide (PLA),” *Polymers*, vol. 11, no. 2, p. 306, 2019.

[3] Y. Wang, Y. Song, J. Du, Z. Xi, and Q. Wang, “Preparation of desirable porous cell structure polylactide/wood flour composite foams assisted by chain extender,” *Materials*, vol. 10, no. 9, p. 999, 2017.

[4] M. T. Zafar, S. Kumar, R. K. Singla, S. N. Maiti, and A. K. Ghosh, “Surface treated jute fiber induced foam microstructure development in poly(lactic acid)/jute fiber biocomposites and their biodegradation behavior,” *Fibers and Polymers*, vol. 19, no. 3, pp. 648–659, 2018.

[5] L. M. Matuana and O. Faruk, “Effect of gas saturation conditions on the expansion ratio of microcellular poly(lactic acid)/wood-flour composites,” *Express Polymer Letters*, vol. 4, no. 10, pp. 621–631, 2010.

[6] H. Naguib, R. Reza, B. Cochrane, H. Naguib, and C. Lee Patrick, “Fabrication and characterization of melt-blended polylactide-chitin composites and their foams,” *Journal of Cellular Plastics*, vol. 47, no. 3, pp. 283–300, 2011.

[7] W. Ding, *Development of Polylactic Acid/Cellulose Nanofiber Biocomposite Foams*, Ph.D Thesis, University of Toronto, Canada, CA, USA, 2016.

[8] Y. Zhang, Lu Cui, H. Xu et al., “Poly(lactic acid)/cellulose nanocrystal composites via the Pickering emulsion approach: rheological, thermal and mechanical properties,” *International Journal of Biological Macromolecules*, vol. 137, pp. 197–204, 2019.

[9] C. Xu, J. Chen, D. Wu, Y. Chen, Q. Lv, and M. Wang, “Polylactide/acetylated nanocrystalline cellulose composites prepared by a continuous route: a phase interface-property relation study,” *Carbohydrate Polymers*, vol. 146, pp. 58–66, 2016.

[10] W. Wan, S. Zhou, and Y. Zhang, “Parallel advances in improving mechanical properties and accelerating degradation to polyactic acid,” *International Journal of Biological Macromolecules*, vol. 125, no. C, pp. 1093–1102, 2019.

[11] N. Pal, P. Dubey, P. Gopinath, and K. Pal, “Combined effect of cellulose nanocrystal and reduced graphene oxide into poly-lactic acid matrix nanocomposite as a scaffold and its antibacterial activity,” *International Journal of Biological Macromolecules*, vol. 95, pp. 94–105, 2017.

[12] P. Dhar, S. S. Gaur, and N. Soundararajan, “Reactive extrusion of polylactic acid/cellulose nanocrystal films for food packaging applications: influence of filler type on thermo-mechanical, rheological, and barrier properties,” *Industrial & Engineering Chemistry Research*, vol. 56, no. 16, pp. 4718–4735, 2017.

[13] T. Kuang, F. Chen, L. Chang, and Y. Zhao, “Facile preparation of open-cellular porous poly(l-lactic acid) scaffold by supercritical carbon dioxide foaming for potential tissue engineering applications,” *Chemical Engineering Journal*, vol. 307, pp. 1017–1025, 2017.

[14] N. Alvarado, J. Romero, A. Torres et al., “Supercritical impregnation of thymol in poly(lactic acid) filled with electrospun poly(vinyl alcohol)-cellulose nanocrystals nanofibers: development an active food packaging material,” *Journal of Food Engineering*, vol. 217, pp. 1–10, 2018.

[15] E. Vatanseyer, D. Arslan, and M. Nofar, “Polylactide cellulose-based nanocomposites,” *International Journal of Biological Macromolecules*, vol. 137, pp. 912–938, 2019.

[16] Z. Han, Y. Zhang, W. Yang, and P. Xie, “Advances in microcellular foam processing of PLA,” *Key Engineering Materials*, vol. 717, pp. 68–72, 2016.

[17] Y. Qiu, Q. Lv, D. Wu, and W. Xie, “Cyclic tensile properties of the polylactide nanocomposite foams containing cellulose nanocrystals,” *Cellulose*, vol. 25, no. 3, pp. 1795–1807, 2018.

[18] S. Sekhar Borkotoky, T. Ghosh, P. Bhagabati, and V. Katiyar, “Polylactic acid/modified gum Arabic (MG) based microcellular composite foam: effect of MG on foam properties, thermal and crystallization behavior,” *International Journal of Biological Macromolecules*, vol. 125, pp. 159–170, 2018.

[19] M. X. Lin, P. P. Zou, and P. Zhang, “Study on foaming properties of PLAINCC: microcellular foam materials,” *Engineering Plastics Application*, vol. 41, no. 10, pp. 90–95, 2013.

[20] A. Ameli, M. Nofar, D. Jahan, G. Rivizi, and C. B. Park, “Development of high void fraction polylactide composite foams using injection molding: crystallization and foaming behaviors,” *Chemical Engineering Journal*, vol. 262, no. C, pp. 78–87, 2015.

[21] G. Wang, G. Zhao, S. Wang, and L. Zhang, “Injection-molded microcellular PLA/graphite nanocomposites with dramatically enhanced mechanical and electrical properties for ultra-efficient EMI shielding applications,” *Journal of Materials Chemistry C*, vol. 6, no. 25, pp. 6847–6859, 2018.

[22] J. Lu, C. Sun, K. Yang, K. Wang, and Y. Jiang, “Properties of polylactic acid reinforced by hydroxyapatite modified nanocellulose,” *Polymers*, vol. 11, no. 6, Article ID 1009, 2019.

[23] A. Karimian, H. Parsian, and M. Majidinia, “Nanocrystalline cellulose: preparation, physicochemical properties, and applications in drug delivery systems,” *International Journal of Biological Macromolecules*, vol. 133, pp. 850–859, 2019.

[24] D. I. Simangunsong, T. H. A. Hutapea, and H. W. Lee, “The effect of nanocrystalline cellulose (NCC) filler on polylactic acid (PLA) nanocomposite properties,” *Journal of Engineering and Technological Sciences*, vol. 50, no. 4, pp. 578–587, 2018.

[25] J. Lu, J. Lang, Na Wang, X. Wang, P. Lan, and H. Zhang, “Preparation and thermostability of hydrophobic modified nanocellulose cellulose,” *Nordic Pulp and Paper Research Journal*, vol. 36, no. 1, pp. 157–165, 2020.

[26] K. Sakakibara, H. Yano, and Y. Tsuji, “Surface engineering of cellulose nanofiber by adsorption of diblock copolymer dispersant for green nanocomposite materials,” *ACS Applied Materials & Interfaces*, vol. 8, no. 37, pp. 24893–24900, 2016.

[27] K. S. Kontturi, K. W. Biegaj, and A. Mautner, “Noncovalent modification and development of biodegradable nano-cellulose nanocrystals,” *Langmuir*, vol. 33, no. 23, pp. 7886–7891, 2017.

[28] A. G. D. Souza, G. F. D. Lima, and R. Colombo, “A new approach for the use of anionic surfactants: Nanocellulose modification and development of biodegradable nanocomposites,” *Cellulose*, vol. 27, no. 10, pp. 5707–5728, 2020.

[29] Y. Yan, H. Amer, T. Rosenau, C. Zollfrank, and o, “Dry, hydrophobic microfibrillated cellulose powder obtained in a
simple procedure using alkyl ketene dimer,” *Cellulose*, vol. 23, no. 2, pp. 1189–1197, 2016.

[30] A. Mulyadi and Y. Deng, “Surface modification of cellulose nanofibres by maleated styrene block copolymer and their composite reinforcement application,” *Cellulose*, vol. 23, no. 1, pp. 519–528, 2016.

[31] J. Sethi, M. Farooq, and S. Sain, “Water resistant nanopapers prepared by lactic acid modified cellulose nanofibers,” *Cellulose*, vol. 25, no. 7, pp. 1–10, 2018.

[32] X. Zhou, X. Lin, and K. L. White, “Effect of the degree of substitution on the hydrophobicity of acetylated cellulose for production of liquid marbles,” *Cellulose*, vol. 23, no. 1, pp. 811–821, 2016.

[33] M. Singh, A. Kaushik, and D. Ahuja, “Surface functionalization of nanofibrillated cellulose extracted from wheat straw: effect of process parameters,” *Carbohydrate Polymers*, vol. 150, pp. 48–56, 2016.

[34] C. Tian, S. Y. Fu, and Q. J. Meng, L. A. Lucia, “New insights into the material chemistry of polycaprolactone-grafted cellulose nanofibers/polyurethane nanocomposites,” *Cellulose*, vol. 23, no. 4, pp. 2457–2473, 2016.

[35] P. Stenstad, M. Andresen, B. S. Tanem, and P. Stenius, “Chemical surface modifications of microfibrillated cellulose,” *Cellulose*, vol. 15, no. 1, pp. 35–45, 2008.

[36] L. Zhou, H. He, and M. Li, “Grafting polycaprolactone diol onto cellulose nanocrystals via click chemistry: e,” *Carbohydrate Polymers*, vol. 189, pp. 331–341, 2018.

[37] M. C. Nongbe, G. Bretel, and L. Ekou, “Cellulose paper azide as a molecular platform for versatile click ligation: application to the preparation of hydrophobic paper surface,” *Cellulose*, vol. 25, no. 2, pp. 1395–1411, 2018.

[38] S. S. Zheng, J. Z. Hang, and X. Y. Sun, “Preparation and properties of phenyltrimethoxysilane modified nanocellulose paper-based barrier coating,” *Polymer Materials Science and Engineering*, vol. 36, no. 3, pp. 120–125, 2020.

[39] J. Lu, P. Askeland, and L. T. Drzal, “Surface modification of microfibrillated cellulose for epoxy composite applications,” *Polymer*, vol. 49, no. 5, pp. 1285–1296, 2008.

[40] H. Khanjanzadeh, R. Behroozi, and N. Bahramifar, “Surface chemical functionalization of cellulose nanocrystals by 3-aminopropyltriethoxysilane,” *International Journal of Biological Macromolecules*, vol. 106, pp. 1288–1296, 2018.

[41] M. Andresen, L. S. Johansson, B. S. Tanem, and P. Stenius, “Properties and characterization of hydrophobized microfibrillated cellulose,” *Cellulose*, vol. 13, no. 6, pp. 665–677, 2006.

[42] S. N. Kasa, M. F. Omar, M. M. Al B. Abdullah, I. Ismail, and T. Ting, “Effect of unmodified and modified nanocellulose reinforced polyactic acid (PLA) polymer prepared by solvent casting method morphology, mechanical and thermal properties,” *Materiale Plastice*, vol. 54, no. 1, pp. 91–97, 2017.

[43] A. Abdulkhani, J. Hosseinzadeh, A. Ashori, S. Dadashi, and T. Takzare, “Preparation and characterization of modified cellulose nanofibers reinforced polyactic acid nanocomposite,” *Polymer Testing*, vol. 35, pp. 73–79, 2014.

[44] W. Jiang, P. Shen, J. Yi, Li Lin, C. Wu, and Ju Gu, “Surface modification of nanocystalline cellulose and its application in natural rubber composites,” *Journal of Applied Polymer Science*, vol. 137, no. 39, Article ID e49163, 2020.

[45] D. Chen, P. Zhang, J. J. Wang, and D. Gao, “Study on the modification degree and properties of acetylated nanocystalline cellulose,” *New Chemical Materials*, vol. 44, no. 01, pp. 146–148+152, 2016.

[46] E. Espino-Pérez, J. Bras, V. Ducruet, A. Guinault, A. Dufrènes, and S. Domenech, “Influence of chemical surface modification of cellulose nanowhiskers on thermal, mechanical, and barrier properties of poly(lactide) based bionanocomposites,” *European Polymer Journal*, vol. 49, no. 10, pp. 3144–3154, 2013.

[47] Q. Xu, Q. Peng, and W. Ni, “Study of different effect on foaming process of biodegradable bionolle in supercritical carbon dioxide,” *Journal of Applied Polymer Science*, vol. 100, no. 4, pp. 2901–2906, 2006.

[48] S. Borkotoky, P. Dhar, and V. Katiyar, “Biodegradable poly(lactic acid)/Cellulose nanocrystals (CNCs) composite microcellular foam: effect of nanofillers on foam cellular morphology, thermal and wettability behavior,” *International Journal of Biological Macromolecules*, vol. 106, pp. 433–446, 2018.

[49] W. D. Ding, T. Kuboki, A. Wong, C. B. Park, and M. Sain, “Rheology, thermal properties, and foaming behavior of high d-content poly(lactic acid)/cellulose nanofiber composites,” *RSC Advances*, vol. 5, no. 111, Article ID 91544, 2015.

[50] J. Jamaluddin, Yul. Hsu, A. Asoh, and U. Uyama, “Effects of acid-anhydride-modified cellulose nanofiber on poly(lactic acid) composite films,” *Nanomaterials*, vol. 11, no. 3, p. 753, 2021.

[51] P. Zhang, H. Yiy, Gao, Y. Cai, and B. Liu, “Hydrolytic and thermal degradation of polyethylene glycol compatibilized poly(lactic acid)-nanocrystalline cellulose bionanocomposites,” *Journal of Applied Polymer Science*, vol. 136, no. 2, Article ID 46993, 2019.

[52] E. F. Sucinda, M. S. A. Abdul Majid, M. J. M. Ridzuan, E. M. Cheng, H. A. Alshahrani, and N. Mamat, “Development and characterisation of packaging film from Napier cellulose nanowhisker reinforced polyactic acid (PLA) bionanocomposites,” *International Journal of Biological Macromolecules*, vol. 187, pp. 43–53, 2021.

[53] S. Borkotoky, T. Ghosh, R. Patwa, and V. Katiyar, “Silk nanocrystal (SNC) reinforced polyactic acid based microcellular foam: impact on porous structure, crystallinity, thermomechanical and surface property,” *Materials Today Communications*, vol. 27, Article ID 102258, 2021.

[54] P. Zhang, P. Zou, and B. Wang, “Preparation and thermomechanical properties of nanocrystalline cellulose reinforced poly(lactic acid) nanocomposites,” *Journal of Applied Polymer Science*, vol. 134, no. 14, Article ID 44683, 2017.

[55] S. Cho, H. Park, S. Y. Yun, and H.-J. Jin, “Influence of cellulose nanofibers on the morphology and physical properties of poly(lactic acid) foaming by supercritical carbon dioxide,” *Macromolecular Research*, vol. 21, no. 5, pp. 529–533, 2013.

[56] C. Xu, J. Chen, D. Wu, Y. Chen, Q. Lv, and M. Wang, “Polylactide/acetylated nanocrystalline cellulose composites prepared by a continuous route: a phase interface-property relation study,” *Carbohydrate Polymers*, vol. 146, pp. 58–66, 2016.

[57] J. Dlouhá, L. Suryanegara, and H. Yano, “The role of cellulose nanofibres in supercritical foaming of polyactic acid and their effect on the foam morphology,” *Soft Matter*, vol. 8, no. 33, pp. 8704–8713, 2012.