Cellulose nanofibrils as templates for the design of poly(L-lactide)-nucleating surfaces

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Abstract

The abilities of surface-grafted cellulose nanofibrils for the nucleation of poly(L-lactide) (PLLA) were investigated. Cellulose nanofibrils with a width of ~3 nm were obtained from wood cellulose via the oxidation using 2,2,6,6-tetramethylpiperidiny1-1-oxyl as a catalyst and successive mechanical treatment. The cellulose nanofibril surfaces were selectively modified with amine-terminated poly(ethylene glycol) chains, via simple ionic bonds. The PEG-grafted cellulose nanofibril/PLLA composite films were prepared using a solvent casting method with chloroform. The isothermal and non-isothermal crystallization kinetics of the PLLA in the composites were studied using differential scanning calorimetry and polarized optical microscopy. The PEG chains were densely immobilized on the surface of the cellulose

nanofibril templates, which had extraordinarily large specific surface areas. As a result, the surface-PEG layers effectively increased the rate of crystallization of the PLLA in the composites. Because of the increased degree of crystallinity after the isothermal crystallization, the composites showed better heat resistance than neat PLLA.

Keywords: Cellulose nanofibril; Polymer nanocomposite; **Crystallization**

1. Introduction

Poly(L-lactide) (PLLA) is one of the most widely used biodegradable polymers. Because of its biocompatibility and renewability, PLLA is attractive for wide range of applications, including packaging [1-3], and medical [4-6] applications. However, a major drawback of PLLA is its low heat resistance. Although the crystallization of PLLA itself is a simple and effective way to solve the problem, the crystallization rate of PLLA is very low. Therefore, the use of neat PLLA typically results in an amorphous or very low-crystallinity material; the resultant material is easily distorted at its glass transition temperature (T_g) of $\sim 60^\circ\text{C}$, which limits its potential for applications.

Much effort has been dedicated to enhancing the crystallization of PLLA. The addition of nucleating agents is an effective method for increasing the crystallization rate of PLLA. Some micro- or nano-elements such as talc [7-9], montmorillonite or nanosilica [10-14], carbon nanotubes [15-17], and graphene [18-20] are known to act as nucleating agents for the crystallization of PLLA. These nucleating agents have large specific surface areas, **which is**

one of the key factors efficiently inducing the crystallization of PLLA on the surfaces.

Organic compounds such as benzenetricarboxylamide derivatives [21] and polysaccharide derivatives [22] have recently been shown to play an effective role as nucleating agents for PLLA. In addition to these nucleating agents, plasticizers such as poly(ethylene glycol) (PEG) can also enhance the crystallization [23-25]. PEG chains increase the polymer chain mobility, which leads to an increase in the crystallization of PLLA via a reduction in the energy required for the chain folding process during crystallization [26,27].

Cellulose nanofibrils are promising candidates for nucleating agents of PLLA from renewable resources, and originate from naturally occurring cellulose microfibrils [28], which have high aspect ratios (>300) with small widths of 2-20 nm and high crystal moduli (130–150 GPa) [29-31]. It has been reported that these nanofibrils act as effective nucleating agents when they are incorporated in semi-crystalline polymers such as PLLA [32-34], polypropylene [35-38], and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [39]. Since the crystallization is initiated on their surfaces, the dispersibility of the nanofibrils in polymer matrices significantly affects the nucleation rate [32,33]. However, it is typically difficult to disperse hydrophilic cellulose nanofibrils in a hydrophobic polymer matrix without any agglomeration.

In our previous study, we showed a method that was used to achieve the individual dispersion of cellulose nanofibrils in a hydrophobic PLLA matrix via the surface modification of 2,2,6,6-tetramethylpiperidiny1-1-oxyl (TEMPO)-oxidized cellulose nanofibrils (TOCNs) [40]. Carboxyl groups are exposed in high densities on the surface of TOCNs [41,42], and

these groups can be used as selective anchoring sites for many kinds of functional groups [43-50]. When long PEG chains are grafted onto the carboxyl groups, the PEG-grafted TOCNs (PEG-TOCNs) can be dispersed at the individual nanofibril level in a PLLA matrix, and the resultant PEG-TOCN/PLLA composites show enhanced mechanical properties with only small amounts of the PEG-TOCNs added.

In this study, we **studied** the nucleating abilities of the PEG-TOCNs for the crystallization of PLLA. TOCNs were prepared from wood cellulose, and the surface carboxyl groups were selectively modified with PEG chains via simple ionic bonds. Two PEGs with different chain lengths were used as grafting agents to evaluate the effects on the nucleating properties. PEG-TOCN/PLLA composites containing 0.5 and 1.0 wt % of TOCNs were prepared by casting and drying mixtures of the PEG-TOCN dispersions and the PLLA solutions in chloroform. The crystallization behavior of the PEG-TOCN/PLLA composites was investigated under isothermal and non-isothermal conditions.

2. Materials and methods

2.1. Materials

A never-dried softwood bleached kraft pulp (Nippon Paper Ind., Japan), which contained approximately 90% cellulose and 10% hemicelluloses, was used as the original wood cellulose. Two amine-terminated PEGs, PEG(23)-NH₂ and PEG(48)-NH₂ (Sunbright MEPA-10H and MEPA-20H with $n = 23$ and $n = 48$, respectively) were obtained from NOF Corp. (Japan). PLLA with $M_w = 94,000$ and $M_n = 45,000$ g mol⁻¹ (Lacty[®]) was supplied from Toyota

Motor Corp., Japan. All other reagents were purchased from Wako Pure Chemicals, Co. Ltd., Japan, and used as received.

2.2. Preparation of PEG-TOCN dispersion in chloroform

TEMPO-oxidized cellulose was obtained according to a previously reported method [40], using the TEMPO/NaBr/NaClO system with 3.8 mmol sodium hypochlorite per gram of cellulose. Oxidation was subsequently carried out with sodium chlorite at pH 4.8, to convert the aldehyde groups still remaining after the TEMPO-mediated oxidation to carboxyls. The TEMPO-oxidized cellulose thus obtained had a carboxylate content of 1.30 mmol g⁻¹, which was determined using conductivity titration. Based on this carboxylate content, the average density of the carboxyl groups on the surface of TOCNs was calculated to be 1.4 groups nm⁻² [40], which was calculated from the width (~3 nm) and carboxylate content (1.3 mmol g⁻¹) of the TOCNs based on the cellulose microfibril model [42]. The TEMPO-oxidized cellulose was then suspended in water at a concentration of 0.1 w/v % consistency. This suspension was homogenized at 7500 rpm for 1 min at room temperature using a double-cylinder-type homogenizer (Physoctron, Microtec Niton Co., Japan); sonication was then performed for 4 min using an ultrasonic homogenizer (US-300T, Nissei, Japan), to obtain a transparent TOCN dispersion with sodium carboxylate groups (TOCN-COONa). The dispersion was centrifuged at 12000 **gravity** for 20 min to remove the small partly fibrillated or unfibrillated fraction (<10%). The width and average length of the TOCNs were 3 nm and 1087 nm, respectively [40]. A 1 M HCl aqueous solution was slowly added to the TOCN-COONa/water dispersion

to form a TOCN gel with free carboxyl groups (TOCN-COOH). The pH of the medium was adjusted to ~2, and stirring was then performed at room temperature for 30 min. The TOCN-COOH gel was collected and washed with water, and solvent exchange to chloroform was achieved through ethanol, using centrifugation. A 1 w/v % solution of PEG-NH₂ in chloroform was added to the TOCN-COOH gel, where the molar ratio of PEG-NH₂ to the carboxyl groups was adjusted to 1:1. The PEG-TOCN/chloroform dispersion was obtained via the application of sonication for 3 min.

2.3. Preparation of PEG-TOCN/PLLA composite films

PEG-TOCN/PLLA composite films were prepared by casting the mixtures of the PLLA solution and the PEG-TOCN dispersion in chloroform (Scheme S1 in Supplementary file). PLLA was dissolved in chloroform with a concentration of 20 mg mL⁻¹. The PLLA solution and PEG-TOCN dispersion were mixed at different ratios, and stirred for 30 min. The mixtures were cast in poly(fluoro acetate) petri dishes and dried at 30°C, and this was followed by vacuum-drying at room temperature for 24 h.

2.4. Analyses

Thermal analysis of the samples was carried out using a Perkin-Elmer differential scanning calorimetry (DSC) 8500 instrument. Samples (2-3 mg) were sealed in aluminum pans. For the non-isothermal crystallization study, the samples were heated to 185°C, maintained at this temperature for 2 min, and then rapidly cooled to 0°C. The parameters were

collected during the second heating run from 0 to 185°C at a heating rate of 20°C min⁻¹. In the isothermal study, samples were heated to 185°C, and then maintained at this temperature for 2 min to erase any thermal history. The samples were then quenched to a desired crystallization temperature (85, 90, 95, 100, 105, 110, 115, and 120°C), and then held at that temperature until the isothermal crystallization was complete. The degree of crystallinity (X_c) of the PLLA after isothermal crystallization for 60 min was calculated from the DSC heating curve using the following equation,

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^\infty} \times 100 \text{ (\%)} \quad (1)$$

where ΔH_{cc} and ΔH_m are the cold crystallization enthalpy and melting enthalpy, respectively, and ΔH_m^∞ is the theoretical melting enthalpy of 100% crystallized PLLA (93.0 J g⁻¹) [51].

Wide-angle X-ray diffraction (WAXD) measurements were carried out using a Rigaku RINT2000 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. The spherulite morphology of the PLLA crystal was observed using a Nikon E600 POL polarized microscope equipped with two hot stages. The sample was initially melted at 185°C for 2 min on one of the stages, and was then immediately transferred to another stage that had been preheated to the desired crystallization temperature (85-120°C). The images were captured using Motic Image Plus 2.2S software. Tensile tests were carried on films with a thickness of ~150 μm using a Shimadzu EZ-TEST tensile tester equipped with a 500 N load cell. Specimens with a length of 30 mm and a width of 2 mm were measured at an extension rate

of 20 mm min⁻¹ with a 10 mm span length. At least 5 specimens were measured for each sample. Thermal mechanical analysis (TMA) was carried out using a 0.03 N load in a nitrogen atmosphere, at temperatures from 30 to 140°C, with a heating rate of 5°C min⁻¹ using a Shimadzu thermomechanical analyzer (Shimadzu, Japan, TMA-60). The change in specimen length with temperature was recorded, and the linear coefficient of thermal expansion (CTE) was calculated.

3. Results and discussion

3.1. Non-isothermal crystallization behavior

The addition of PEG(23)-TOCN and PEG(48)-TOCN significantly increased the crystallization rate of PLLA under heating. The cold crystallization peaks of PLLA became sharp, and the cold crystallization temperature (T_{cc}) decreased from 134 to 120 and 111°C by the addition of 1.0% PEG(23)-TOCNs and PEG(48)-TOCNs, respectively (Table 1 and Fig. 1).

Fig. 1. DSC curves for PLLA, the 1.0% PEG-TOCN/PLLA composites, and the PEG/PLLA blends in the second heating run (heating rate: 20°C min⁻¹).

Table 1

Thermal properties of PEG-TOCN/PLLA composites and PEG/PLLA blends in the second heating run (heating rate: 20 °C min⁻¹).

Sample	Weight content (wt %)		T_g	T_{cc}	ΔH_{cc}	T_m	ΔH_m
	TOCN	PEG	(°C)	(°C)	(J g ⁻¹)	(°C)	(J g ⁻¹)
Neat PLLA	0	0	58.3	134.0	10.6	160.0	10.6
1.0% PEG(23)- TOCN/PLLA composite	1.0	1.5	50.5	120.0	39.8	157.5 162.2	39.8
PEG(23)/PLLA blend	0	1.5	48.9	129.3	10.5	158.8	10.5
1.0% PEG(48)- TOCN/PLLA composite	1.0	3.0	51.9	111.3	40.8	155.5 162.5	40.9
PEG(48)/PLLA blend	0	3.0	49.1	129.5	19.0	158.3	19.0

T_g : glass transition temperature, T_{cc} : cold crystallization temperature, ΔH_{cc} : cold crystallization enthalpy, T_m : melting temperature, ΔH_m : melting enthalpy. ΔH_{cc} and ΔH_m were calculated based on the weight contents of the PLLA component.

In this study, the weight contents were based on the contents of TOCN without PEG moieties. The cold crystallization enthalpy (ΔH_{cc}) increased with increasing PEG-TOCN contents. In contrast, no such nucleating effect was observed in the PEG/PLLA blends (without TOCN) at these weight contents. The T_g of the PLLA matrix decreased with increasing PEG contents. Moreover, the melting peak of pure PEG molecules at ~55°C (Fig. S1 in Supplementary file) was not observed at all in the DSC curves of Fig. 1, which showed that the PEG chains were sufficiently miscible in the PLLA matrix in this system.

PEG chains are typically used as a plasticizing agent for PLLA, and can significantly

increase the cold crystallization rate of PLLA (by >10 wt %) [23-25]; the PEG chains enhance the chain mobility of PLLA as the density of PEG chains increases, which leads to a reduction in the energy required for the chain folding process during crystallization [26,27]. In this study, the PEG chains, which were not immobilized on the surface of the TOCNs, did not enhance the cold crystallization at all, probably due to the low PEG density in the matrix. However, when the PEG chains were densely anchored on the TOCN surfaces (~ 1.4 chains nm^{-2}), the chains significantly enhanced the crystallization rate of the PLLA; the rate increased as the PEG content in the composite films was increased (Table 1). This demonstrated that the sufficiently dispersed PEG-TOCN elements with large surface areas efficiently initiated the nucleation of PLLA. Moreover, because PEG(48)-TOCN/PLLA had a T_{cc} (111°C) lower than that of PEG(23)-TOCN/PLLA (120°C), the PLLA mobility may have been increased by the dense PEG layers on the TOCN surfaces, which resulted in a reduction in the energy required during crystallization. In addition, double melting behavior was observed in the PEG-TOCN/PLLA composites (Fig. 1), which is explainable in terms of melting-recrystallization-remelting phenomenon.

3.2. Isothermal crystallization behavior

The isothermal crystallization behavior of the composites was investigated using DSC. Neat PLLA and the PEG-TOCN/PLLA composites were melted at 185°C for 2 min, and subsequently cooled to different isothermal crystallization temperatures (T_c). Figure 2 shows the crystallization half-time ($t_{1/2}$) as a function of the crystallization temperature T_c , which

ranged from 85 to 120°C. $t_{1/2}$ is defined as the time at which the relative crystallinity (X_t) reaches 50% of the total crystallinity, and can be calculated using the following equation,

$$X_t = \frac{\int_0^t (dH / dt) dt}{\int_0^\infty (dH / dt) dt} \times 100 \quad (\%) \quad (2)$$

Fig. 2. The crystallization half time ($t_{1/2}$) of the PLLA film, and the 1.0% PEG(23)-TOCN/PLLA and 1.0% PEG(48)-TOCN/PLLA composite films.

The addition of PEG-TOCN enhanced the isothermal crystallization of PLLA to a remarkable degree. At any T_c , the $t_{1/2}$ of PLLA decreased with the addition of PEG-TOCN (Fig. 2). The minimum $t_{1/2}$ value for the neat PLLA and the PEG-TOCN/PLLA composites was observed at approximately 100°C. PEG(23)-TOCN/PLLA and PEG(48)-TOCN/PLLA showed a minimum $t_{1/2}$ of 4.8 and 4.7 min, respectively, at 105°C, whereas that of PLLA was 10.6 min. These values are comparable with those of PLLA composites containing 1% silylated cellulose crystals ($t_{1/2} = 4.2$ min at 110 °C) [33] and those of composites containing

1% nanocellulose prepared by aqueous counter collision ($t_{1/2} = 3.4$ min at 130 °C) [36]. In contrast, when only PEG molecules without TOCNs were added to the PLLA matrix, the enhancement in isothermal crystallization was not as significant as that achieved using the PEG-TOCNs (Table S1 in Supplementary file). Thus, the isothermal crystallization of PLLA was effectively enhanced by PEG-TOCNs.

The crystallization kinetics of the samples were described using the well-known Avrami theory [51-53]. In the Avrami equation, X_t is described as,

$$X_t = 1 - \exp(-kt^n) \quad (3)$$

where n is the Avrami exponent and k is the rate constant of crystallization. In this equation, n is dependent on the crystal shape and the nucleation process. Equation (3) can be rearranged to give the following equation,

$$[-\ln(1-X_t)] = \ln k + n \ln t \quad (4)$$

The parameter n can be obtained from the slope of plots of $\ln[-\ln(1-X_t)]$ versus $\ln t$.

Figure 3 shows isothermal crystallization curves for neat PLLA and PEG-TOCN/PLLA composites at 95, 105, and 115°C and the corresponding Avrami plots. The isothermal peaks became sharper after the addition of the PEG-TOCNs, which clearly showed that they enhanced the isothermal crystallization of PLLA. The n and X_c values obtained from the isothermal peaks are listed in Table 2. The Avrami exponent n was obtained using a linear fitting of the X_t data in the range of 20-70%. This exponent predicts the nucleation mechanism and growth dimensions. For the neat PLLA, n was close to 4, indicating homogeneous nucleation with a three-dimensional growth [54]. In contrast, the n values of the PEG-

TOCN/PLLA composites were in the range of 2.2-2.7, which indicated that the growth of the PLLA crystals occurred with heterogeneous nucleation in two or three dimensions.

Fig. 3. Isothermal crystallization curves obtained using DSC, and corresponding Avrami plots of $\ln[-\ln(1-X_t)]$ versus $\ln(t)$ at different temperatures: (a, d) 95°C, (b, e) 105°C, and (c, f) 115°C.

The crystal growth of the neat PLLA and PEG-TOCN/PLLA composites was observed using polarized optical microscopy at different T_c values (Fig. 4). The PEG-TOCN/PLLA composites showed a significantly higher nucleation density than the neat PLLA, because the nucleation was enhanced on the TOCN surfaces. Moreover, no spherulites were observed for the composites; this was different from the behavior observed for the neat PLLA. This was likely because the dense PEG-TOCN networks in the composites prohibited the three-dimensional growth of the PLLA spherulites in the composites. In a previous study, it was demonstrated that TOCNs with a width of ~3 nm and a length of ~1 μm formed a network

throughout a polymer matrix (i.e., via percolation) with a TOCN content of only 0.31 vol % (0.5 wt %) [55].

Fig. 4. Optical micrographs of neat PLLA and 1.0% PEG-TOCN composites observed between crossed polarizers after isothermal crystallization for 10 min at 95, 105, and 115°C. The scale bar represents 100 μ m.

In this study, it is likely that dense TOCN networks were formed in the composites with 1.0 wt % TOCN contents. As a result, the TOCN network in the PLLA matrix restricted the dimensionality of the crystal growth of PLLA (which is consistent with the lower n values of the composites, as discussed previously). The size of the PLLA spherulites in the neat PLLA films increased with crystallization temperature, and the nucleation rate was lower (Fig. S2 in Supplementary file). In contrast, the crystal size in the PEG-TOCN/PLLA composites was apparently unchanged with temperature in the presence of the TOCN networks. The X_c value increased up to 42.1 % with the addition of PEG-TOCNs (Table 2), which is as high as those

of PLLA composites containing 25 w/w % microcrystalline cellulose ($X_c = 44.5\%$) [56]. The WAXD patterns showed that the addition of PEG-TOCNs did not change the crystal forms of the neat PLLA at all during isothermal crystallization (Fig. S3 in Supplementary file). Thus, the PEG-TOCNs increased not only the crystallization rate but also the X_c of PLLA, without changing the crystal structure.

Table 2

Isothermal crystallization kinetics parameters at 95, 105, and 115°C.

Sample	$T_c = 95^\circ\text{C}$		$T_c = 105^\circ\text{C}$		$T_c = 115^\circ\text{C}$	
	n	$X_c (\%)$	n	$X_c (\%)$	n	$X_c (\%)$
Neat PLLA	3.4	28.5	3.5	32.2	3.7	30.2
0.5% PEG(23)-TOCN	2.7	32.4	2.8	37.0	2.4	38.0
1.0% PEG(23)-TOCN	2.4	33.6	2.4	39.5	2.7	41.7
0.5% PEG(48)-TOCN	2.4	32.6	3.0	37.1	2.4	39.6
1.0% PEG(48)-TOCN	2.2	33.7	2.6	40.1	2.3	42.1

The thermal dimensional stability of the films after isothermal crystallization at 95, 105, and 115°C for 5 min was evaluated using thermomechanical analysis. The composites exhibited better thermal stability than neat PLLA, due to the increased crystallinity (Fig. 5a). The thermal expansion of the neat PLLA film increased above the T_g of ~60°C. In contrast, the thermal expansion values of the composite films were smaller than 4% in this temperature range. The CTE values of the composites decreased significantly (by approximately one order of magnitude) after the isothermal crystallization, whereas the neat PLLA showed a modest

decrease in its CTE (Fig. 5b). The PEG-TOCN/PLLA composites had CTE values of ~230 ppm K⁻¹ after crystallization, which is comparable with those of xylan-ester/PLLA composites (214 ppm K⁻¹) [22]. This was primarily due to the increased degree of crystallinity of the PLLA in the composites. The Young's moduli of the samples increased as the degree of crystallinity increased (Fig. S4 and Table S2 in Supplementary file). However, the crystallization resulted in brittle failure as has been reported previously [25,57,58].

Fig. 5. (a) Thermal expansion behavior and (b) the CTE above T_g of neat PLLA and 1.0% PEG-TOCN/PLLA composites after isothermal crystallization at 95, 105, and 115°C for 5 min.

4. Conclusions

In this study, we demonstrated the potential of PEG-TOCNs as a bio-based nucleating agent for PLLA. The addition of PEG-TOCNs to PLLA matrix significantly increased the crystallization rate of PLLA under heating. The PEG chains densely immobilized on the surface of the TOCNs nanodispersed in PLLA matrix were likely to increase the effective nucleation rate of PLLA. The isothermal crystallization curves obtained using DSC and corresponding Avrami plots of the PEG-TOCN/PLLA composites revealed that the growth of the PLLA crystals occurred with homogeneous nucleation in one or two dimensions in the composites. The dense TOCN networks were likely to form in the composites, resulting that the TOCN network in the PLLA matrix restricted the dimensionality of the crystal growth of PLLA. The composites exhibited better thermal stability than neat PLLA, due to the increased crystallinity; the thermal expansion values of the composite films were smaller than 4%. We expect therefore that the surface-modified cellulose nanofibrils are useful as an effective template for the design of nucleating surfaces for biopolymer matrices.

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Supplementary data

Supplementary data related to this article can be found, in the online version, at
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Graphical Abstract

Cellulose nanofibrils as templates for the design of poly(L-lactide)-nucleating surfaces

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