Research article

Melt spinnabilities of thermoplastic paramylon mixed esters

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ABSTRACT

The low thermoplasticities of polysaccharide esters make them unsuitable for melt spinning. In this study, we aimed to overcome this problem by mixed esterification of paramylon, a euglenoid β-1,3-glucan with short- and medium-chain acyl groups, as melt-spinning materials. Thermal analyses revealed that all the synthesized paramylon mixed esters exhibited glass transition temperatures greater than 100 °C; some of them showed large differences between the melting and 5%-weight-loss temperatures (Td5s) and are extrudable through a spinneret at a temperature ~100 °C below Td5, rendering them potential candidates for the production of melt-spun filaments. Among the various compounds investigated, paramylon acetate propionates, in which the degrees of acetyl- and propionyl-group substitution were 0.5–0.7 and 2.2–2.5, respectively, could be melt-spin to yield mechanically tough crystalline monofilaments. In contrast, the melt spinning of cellulose acetate propionate, analogous to the paramylon acetate propionates in terms of acyl substituents, their substitution degrees, and molecular weights, but differs from it in terms of the glucose linkage mode (i.e., β-1,3 vs β-1,4), yielded brittle, charred, and short filaments. Curdlan acetate propionate, another analogue with a degree of polymerization five times larger than that of paramylon mixed esters, was not extrudable due to the lack of thermoplasticity. Therefore, we herein confirmed the superiority of paramylon as a primary raw material for melt-spun filaments.

1. Introduction

Thermoforming is a useful technique for molding products of various forms from thermoplastic polymers (Throne, 2008). Owing to depletion of global petroleum reserves, there is increasing interest in replacing petroleum-based thermoplastics with those derived from renewable resources. Unfortunately, polysaccharides are unsuitable for this purpose because they do not exhibit the desired degree of thermoplasticity; hence, polysaccharides need to be chemically modified (Erdmann et al., 2014; Zepnik et al., 2013). Acylation with a short-chain fatty acid, such as acetic acid, is a typical method used to chemically modify cellulose, the most abundant natural polysaccharide. However, the narrow process window, which ranges from the melting temperature to the decomposition temperature, prevents successful thermoforming of thermoplastic acetylated cellulose derivatives. This necessitates the use of a large amount of plasticizer, which can reduce the mechanical strength and heat resistance of the final product (Park et al., 2004; Toyama et al., 2015). The aforementioned problem is encountered in melt spinning, a thermoforming technique for producing monofilaments, as well as in other techniques, particularly when an acylated cellulose derivative is used as the raw material. To circumvent this problem, a combination of cellulose mixed esters (cellulose acetate propionates (CAPs) and cellulose acetate butyrate (CABs)) and a water-washable plasticizer have been employed (Aranishi et al., 2006). Hooshmand et al. prepared continuous fibers based on CAB using cellulose nanocrystals and triethyl citrate as additives, in order to improve the mechanical strength and thermoplasticity (Hooshmand et al., 2014). Although these thermoforming methods are efficient, they render the production process more complex. Both CAP and CAB are commercially available and commonly used thermoplastic cellulose mixed esters. Given that the thermoplasticity of a CAP likely stems from its lower degree of polymerization (DP) (= Mw/molecular weight of acyl-substituted glucose unit), which ranges from ~140 to 300, as well as mixed esterification (Aranishi et al., 2006), we hypothesized that there is room to improve these mechanical properties. Owing to the high hydroxyl group contents of CABs (4.8 wt%), which enables their dissolution in alcohols (Hooshmand et al., 2014), we also expected cellulose mixed-ester-based monofilaments to show low alcohol and water resistances. We believe that these potential issues are inherent to the use of cellulose.

Our approach to the preparation of polysaccharide-based...
monofilaments through melt spinning involves the use of paramylon, a linear β-1,3-glucan from *Euglena*, as the main chain of the thermoplastic polysaccharide. We expected paramylon mixed esters to exhibit better thermoplasticity during melt spinning than cellulose, a β-1,4-glucan, upon chemical modification, because of the following reasons. First, the narrow polymer chain-length distribution of paramylon (polydispersity index = weight-average molecular weight (\(M_\text{w}\))/number-average molecular weight (\(M_\text{n}\) ≈ 1.2)) would cause its derivatives to melt within a small temperature range. Second, there are large differences (~100 °C) between the melting (\(T_m\)) and the 5% weight-loss temperatures (\(T_{5\%}\)) of paramylon acetate propionate, paramylon acetate butyrate, paramylon acetate pentanoate, and paramylon acetate hexanoate. Such temperature difference facilitates melting of the paramylon mixed esters without charring (Shibakami and Sohma, 2017). Third, we expected that the linear polymeric structures of β-1,3-glucans facilitate greater degree of thermoplasticization than the structurally analogous β-1,4-glucans, such as cellulose, because they prevent excessive polymer entanglement. Alternatively, the polymer chains exhibit well-ordered alignment in the solid state owing to the helicity of the β-1,3-bond. Fourth, paramylon is more favorable as a backbone of thermoplastics than curdlan, a structurally analogous β-1,3-glucan, because its molecular weight, which is three times larger than that of paramylon, obstructs thermoplasticization (Shibakami and Sohma, 2017). Therefore, we hypothesized that thermoplastic paramylon mixed esters can be transformed into mechanically tough monofilaments more readily than the structurally analogous β-1,4-glucans and curdlan if their physical properties, such as surface tension, viscosity, and elasticity in the molten state, and spinning conditions including temperature, extruding force, and speed, are balanced for melt spinning (Nakagawa, 1952a, 1952b).

The main purpose of this study was to elucidate the chemical structures of thermoplastic paramylon mixed esters that exhibit balance between thermoplasticity for melt spinability and ability to form mechanically tough filaments. In this study, cellulose acetate propionate, curdlan acetate propionate, and eleven candidate paramylon mixed esters, with different acyl chain lengths, acyl group degrees of substitution (DS), and acyl group combinations, were synthesized. Their structural and thermal properties were then characterized. Candidates for melt-spin filament materials chosen from among these compounds via preliminary manual melt spinning were paramylon acetate propionates having low acetyl DS and high propionyl DS. We confirmed that the compounds are transformable to monofilaments via mechanical melt spinning. The mechanical, thermal, and X-ray diffraction analyses indicate that these filaments are crystalline in character and their mechanical properties are comparable to those of practically used cellulose-based filaments. The advantages of melt spinning that is applicable to the thermoplasticity during melt spinning than cellulose, because they prevent excessive polymer entanglement.

### 2. Experimental

#### 2.1. General methods

The 

The 1H and 13C nuclear magnetic resonance (NMR) spectra of the products were obtained using a Bruker AVANCE 500 spectrometer (500 MHz). The Fourier-transform infrared (FT-IR) spectra of the thin films of polysaccharide mixed ester solids formed by hot pressing (~50 mg, 230 °C, 10 MPa, 10 s) were obtained using a JASCO FT/IR-4080T spectrophotometer equipped with an attenuated total reflectance accessory (ZnSe prism, ATR Pro 400-S, JASCO) with a resolution of 4 cm⁻¹. The DS, which is defined as the average number of functional groups attached to a glucose unit, was determined by comparing the integrated value of methyl/methylene protons of the medium-chain acyl and acetyl groups with that of the glucose protons in the 1H NMR spectrum; DSac and DSme represent the DS values of the acetyl and medium-chain acyl groups (i.e., propanoyl, butanoyl, pentanoyl, and hexanoyl), respectively. All the chemicals and reagents were obtained commercially and were used without purification. Paramylon was obtained from *Euglena gracilis* strain EOD-1 (FERM BP-11530). The 1H NMR, 13C NMR, and FT-IR data, and the \(M_\text{w}\) and \(M_\text{n}\) of paramylon are as follows: 1H NMR (1.0 M NaOD/D₂O) δ 4.72 (m, 1H; H1), 3.93–3.45 (m, 6H; H2–H6); 13C NMR (1.0 M NaOD/D₂O) δ 106.3 (C1), 89.9 (C3), 79.6 (C5), 76.6 (C2), 72.3 (C4), 64.1 (C6); FT-IR (cm⁻¹) 3361, 2899, 1118, 1078, 1040, 885; \(M_\text{w}\) = 1.892 × 10⁶ and \(M_\text{n}\) = 1.531 × 10⁵ (Shibakami and Sohma, 2017). Dissolving pulp (α-cellulose ‘92%, NDFS, estimated \(M_\text{w}\) = 3.285 × 10⁶ (Shibakami and Sohma, 2017)) was obtained from Nippon Paper Industries Co., Ltd. Curdlan was purchased from Fujifilm Wako Pure Chemical Corporation. Cellulose acetate butylate (\(M_\text{w}\) ~ 30,000) (CAB) was purchased from Sigma-Aldrich. The \(D_{\text{Sac}}\), \(D_{\text{Sm}}\), \(T_g\), \(M_\text{w}\), and \(M_\text{n}\) of CAB determined herein are 0.36, 2.64, 97.1 °C, 5.298 × 10⁴ (3), and 3.626 × 10⁵ (3), respectively.

#### 2.2. Synthesis of paramylon mixed esters

Paramylon mixed esters (products 1a–1d, 2, 3, 4a, 4b, 5–7) were synthesized according to our previously reported method (Shibakami and Sohma, 2017). The procedure, as well as that for the syntheses of cellulose acetate propionate (product 8) and curdlan acetate propionate (product 9), is described in the Supplementary Material.

##### 2.2.1. Paramylon acetate propionate from acetic acid and propionic anhydride (1a) (feed molar ratio = 1:3)

A mixture of paramylon (15.007 g, 92.56 mmol), LiCl (11.738 g, 276.90 mmol), and N,N-dimethylacetamide (DMAC) (750 mL) was heated at ~100 °C for ~0.5 h under nitrogen. To the resulting homogeneous solution, 4-dimethylaminopyridine (2.159 g, 17.67 mmol) was added in a single portion. Subsequently, a solution prepared by heating a mixture of acetic acid (12.590 g, 204.66 mmol) and propionic anhydride (81.391 g, 625.41 mmol) at ~110 °C for 1 h under nitrogen was added dropwise. After stirring the reaction mixture at ~100 °C for 3 h, methanol (750 mL) was added. The mixture was then added dropwise to water (3.0 L), resulting in the formation of a white precipitate. This precipitate was separated by decantation and dispersed in chloroform (500 mL), and the heterogeneous mixture was stirred overnight using a mechanical stirrer at ambient temperature. After removing the aqueous layer, the nearly homogeneous mixture was poured into ethanol (1.5 L) to obtain a white precipitate. This precipitate, and the one produced by allowing the ethanol solution to stand overnight, were combined, dispersed in chloroform (350 mL), and mechanically stirred at ambient temperature overnight. The resulting homogeneous solution was poured into ethanol (1.5 L) to yield a white precipitate. This purification process was repeated twice. Air drying overnight and vacuum drying (~60 °C, 8 h) yielded the desired product (1a) as a white solid (25.268 g, 77.54 mmol, Yield: 84.3%). The successful synthesis of 1a was confirmed by 1H NMR and FT-IR spectroscopies: 1H NMR (CDCl₃) δ 4.86 (brs), 4.80 (brs), 4.29 (brs), 4.02 (brs), 3.71 (brs), 3.59 (brs), 2.51–1.99 (m), 1.18–0.19 (m); \(D_{\text{Sac}}\), 0.46; \(D_{\text{Sm}}\), 2.54; 13C NMR (CDCl₃) δ 174.0, 172.5, 172.3, 170.6, 169.1, 168.9, 100.7, 78.2, 72.7, 72.2, 68.1, 62.1, 27.3, 20.7, 8.9; FT-IR (cm⁻¹) 2976, 2973, 1365, 1218, 1045, 1104, 870, 807.

#### 2.3. Size exclusion chromatography

The polysaccharide mixed esters were subjected to size exclusion chromatography using a gel permeation chromatography column (KD-805, Shodex) (elution solvent: chloroform, elution temperature: 40 °C, elution solvent flow rate: 1.0 mL/min). The chromatography system was equipped with a multi-angle static light-scattering set-up combined with a multi-angle laser photometer (miniDAWN, Wyatt Technology), a dynamic light-scattering module (WyattQELS, Wyatt Technology), and a refractive index detector (Optilab rEX, Wyatt Technology). The solutions for analysis were prepared by dissolving the polysaccharide mixed esters.
in chloroform and purified through a 0.20-μm filter prior to injection. The concentration was ~4.0 mg/mL, the injection volume was 100 μL, and the refractive index increment (dn/dc) was 0.0372.

2.4. Thermal analysis

The melting behavior of the ethanol-precipitated solids was preliminarily observed using a melting point apparatus (MP-500D, Yanako). The T_m, glass transition temperature (T_g), and enthalpy change (ΔH) were determined from the differential scanning calorimetry (DSC) thermograms obtained using a calorimeter (Thermo plus EVO2 DSC 8230, Rigaku). Each ethanol-precipitated solid (~6 mg) was mechanically sealed in an aluminum pan and heated from 25 to 230 °C (10.0 °C/min) and held at 230 °C for 5 min. After cooling from 230 to 25 °C (5.0 °C/min) and holding at 25 °C for 5 min, the test sample was heated to 250 °C at the same scan rate. The thermogram obtained during the first heating step was used to determine T_m, whereas that obtained during the second heating step was used to determine T_g and ΔH. Furthermore, thermogravimetric analysis was performed on the ethanol-precipitated solids using a thermogravimetric (TG) analyzer (Thermo plus EVO2 TG 8120, Rigaku) to determine the T_d5 value. Each sample was heated from 25 to 500 °C (10.0 °C/min) under flowing nitrogen (100 mL/min). Isothermal stability of the ethanol-precipitated solids was evaluated using thermogravimetric analysis, in which the sample weight was continuously measured upon isothermal heating (246 ± 1.0 °C, 30 min). To obtain the thermal properties of the melt-spun filaments, they were subjected to DSC analysis using the same heating/cooling program used for the ethanol-precipitated solids.

2.5. Melt volume flow rate (MVR) measurements

MVR measurements were performed using a melt indexer (IMC-E0F0, Imoto). Briefly, ~1.0 g of the polysaccharide mixed ester solid was placed in the cylinder (length of 100 mm, and outer and inner diameters of 50.0 and 7.0 mm, respectively) of the melt indexer and heated at different temperatures (210, 220, 230, 240, and 250 °C) for 3 min. The melted solid was then extruded from the cylinder through a die orifice (length of 10 mm, and outer and inner diameters of 7.0 and 1.0 mm, respectively) using a 37.26-, 49.03-, or 98.07-N weight. The MVR was calculated by measuring the volume of the solid extruded through the orifice.

\[
\text{MVR (cm}^3/10 \text{min)} = \left( \frac{A \times t_{\text{ref}}}{L \times t} \right)
\]

where A is the cross-sectional area of the orifice (0.407 cm²), t_{ref} is the base time (600 s), L is the stroke length of the piston (1.25 cm), and t is the stroke time of the piston (s).

2.6. Melt spinning

Melt spinning was performed using a custom-built spinning system comprising the melt indexer (IMC-E0F0, Imoto) used for MVR measurement and a spinning apparatus (IMC-1128, Imoto). Briefly, ~1.0 g of the solid polysaccharide mixed ester was placed in the cylinder and heated at different temperatures (160, 240, 245, and 250 °C) for 3 min. The melted solid was then extruded from the cylinder through a spinneret (same as the orifice for melt spinning) using a 37.26- or 98.07-N weight. The extruded monofilament was quickly air-cooled and spun using the spinning apparatus with a roll of diameter 90 mm (mechanical spinning) or by hand (manual spinning).

The monofilament fineness (in dtex) was determined by dividing the length of the filament by its weight.

2.7. Mechanical strength measurements

Tensile tests were performed on the melt-spun monofilaments using a universal tester (Tensilon RTG-1225, A&D) at room temperature. The initial distance between the chucks was set at 30 mm, and the pulling rate was 3 mm/min. The number of samples tested in each case was more than 50.

2.8. Scanning electron microscopy (SEM)

The monofilaments were fixed on the metal stage of the microscope using a carbon conductive double-sided tape. Images were acquired under high vacuum using a scanning electron microscope (JSM-6060, JEOL) operated at an accelerating voltage of 2.5 kV.
2.9. Wide-angle X-ray diffraction (WAXD)

WAXD experiments were performed using an X-ray diffractometer (RINT-2550V, Rigaku) with monochromatic Cu-Kα radiation (λ = 0.15418 nm) generated at 40 kV and 200 mA through an optical slit system (divergence slit angle = 0.5°/C, scattering slit angle = 0.5°/C, and receiving slit = 0.3 mm). Scattering was performed over the scattering angle (2θ) range 2–60° at a step size of 0.05°/C and scan rate of 5°/min.

2.10. Dynamic mechanical analysis (DMA)

DMA was performed on the monofilaments (length = 20 mm, diameters = 176, 153, and 113 μm) using a dynamic mechanical analyzer (RSA-G2, TA Instruments). The dynamic moduli of the monofilaments were measured at 0.1% strain and 1 Hz from 30 to 150 °C at a heating rate of 5 °C/min. The axial force was adjusted to 0.15 N, and a strain adjust of 15% was set with a minimum strain of 0.01%, maximum strain of 1%, and minimum force of 0.01 N to prevent the samples from

| Table 1 |
|---|
| Polymeric structural parameters of polysaccharide mixed esters. |
| Product | R<sub>1</sub> | R<sub>2</sub> | Feed molar ratio of A/AA | DS<sub>ace</sub> | DS<sub>mc</sub> | M<sub>w</sub> (× 10<sup>5</sup>) | M<sub>n</sub> (× 10<sup>5</sup>) | M<sub>w</sub>/M<sub>n</sub> | DP |
| 1a | CH<sub>3</sub> | CH<sub>3</sub> | 1/3 | 0.46 | 2.54 | 4.615 (0.8)<sup>a</sup> | 3.504 (0.8) | 1.317 (1.0) | 1416 |
| 1b | CH<sub>3</sub> | CH<sub>3</sub> | 1/2 | 0.72 | 2.24 | 4.680 (0.8) | 3.561 (1.0) | 1.314 (1.0) | 1462 |
| 1c | CH<sub>3</sub> | CH<sub>3</sub> | 1/1 | 1.03 | 1.96 | 3.990 (1.0) | 3.174 (2.0) | 1.257 (3.0) | 1257 |
| 1d | CH<sub>3</sub> | CH<sub>3</sub> | 2/1 | 1.50 | 1.25 | 5.029 (0.5) | 3.938 (0.6) | 1.277 (0.7) | 1692 |
| 2 | CH<sub>3</sub> | CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub> | 1/1 | 1.24 | 1.71 | 4.467 (0.4) | 3.628 (0.5) | 1.568 (1.0) | 1329 |
| 3 | CH<sub>3</sub> | CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub> | 1.2/1 | 1.24 | 1.73 | 5.042 (0.8) | 3.957 (2.0) | 1.274 (2.0) | 1394 |
| 4a | CH<sub>3</sub>CH<sub>2</sub> | CH<sub>3</sub> | 1/2 | 1.82 | 0.90 | 4.148 (0.7) | 3.178 (1.0) | 1.305 (1.0) | 1364 |
| 4b | CH<sub>3</sub>CH<sub>2</sub> | CH<sub>3</sub> | 2/1 | 1.20 | 1.33 | 3.329 (1.0) | 2.321 (2.0) | 1.419 (3.0) | 1146 |
| 5 | CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub> | CH<sub>3</sub> | 1/1 | 2.32 | 0.65 | 3.642 (0.4) | 3.007 (0.6) | 1.211 (0.7) | 1029 |
| 6 | CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub> | CH<sub>3</sub> | 1/2 | 2.52 | 0.41 | 5.156 (0.5) | 4.348 (0.5) | 1.186 (0.7) | 1311 |
| 7 | CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub> | CH<sub>3</sub> | 1/2 | 2.52 | 0.45 | 3.615 (0.4) | 3.109 (0.5) | 1.333 (1.0) | 840 |
| 8 | CH<sub>3</sub> | CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub> | 1/3 | 0.54 | 2.46 | 5.671 (4.0) | 2.527 (2.0) | 2.244 (5.0) | 1746 |
| 9 | CH<sub>3</sub> | CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub> | 1/3 | 0.40 | 2.46 | 25.47 (4.0) | 21.66 (5.0) | 1.176 (7) | 7925 |
| CAB | CH<sub>3</sub> | CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub> | – | 0.36 | 2.64 | 5.398 (3) | 0.3626 (3) | 1.461 (4) | 145 |

A, acid; AA, acid anhydride.

<sup>a</sup> Values in parentheses indicate percentage errors.

Fig. 1. DSC thermograms of ethanol-precipitated polysaccharide mixed esters: (a) first and (b) second heating scans.
buckling or exceeding the specified strain. A force tracking mode was set such that the axial force was thrice the magnitude of the oscillation force.

3. Results and discussion

3.1. Design and synthesis of paramylon mixed esters

For polysaccharide esters, the thermoplasticization and reinforcing effects of acylation exhibit an inverse relationship, i.e., the longer the acyl chain, the higher is the thermoplasticization effect but the lower is the mechanical strength of the final product (Marubayashi et al., 2014; Puanglek et al., 2017). Hence, the primary objective of this study was to determine the combination of length, DS range, and acyl group that would make the paramylon thermoplasticity suitable for melt spinability and endow it with the ability to form mechanically robust monofilaments that circumvent the need for plasticizers. With this goal in mind, we synthesized eleven paramylon mixed esters with varying combinations of two acyl groups and DS values.

The reactions involved in the synthesis of the paramylon mixed esters, 8, and 9 are modified versions of previously reported reactions (Shibakami and Sohma, 2017) (Scheme 1). All the products contain an acetyl group as the shorter chain because substitution with the smallest acyl group (the acetyl group) contributes to mechanical robustness. At the same time, this substitution reduces thermoplasticity. However, thermoplasticity for melt spinability and mechanical toughness of filaments can be simultaneously achieved if the chain length and DS of the medium-chain acyl groups are optimized. Briefly, a mixture of acid anhydrides is produced by the reaction between a fatty acid (acetic, propionic, butyric, or hexanoic acid) and an acid anhydride (acetic, propionic, butyric, or pentanoic anhydride) (Reaction 1). The acid anhydrides then react with either paramylon, cellulose from dissolving pulp, or curdlan to yield products 1–9 (Reaction 2). Specifically, paramylon was treated with acid anhydrides obtained from a mixture of acetic acid and propionic anhydride (1a–1d) or propionic acid and acetic anhydride (4a, 4b), at different molar feed ratios, to produce paramylon acetate propionates having various DS values. Since the content ratio of the acylating reagent (acid anhydride) depends on the combination of the fatty acid and acid anhydride as well as the corresponding molar feed ratio, these synthesis conditions should provide paramylon acetate propionates with a wide variety of DS values. We anticipated that these products would be the most promising candidates because they contained the shortest and the second-shortest acyl groups.

Table 1 shows the DS values of the synthesized products and CAB. As expected, those of the paramylon acetate propionates (1a–1d, 4a, 4b) vary widely; specifically, 0.46–1.82 for DSace and 0.90–2.54 for DSinc. Both paramylon acetate butyrates 2 and 5, and paramylon acetate pentanoates 3 and 6 have two different DS combinations: medium-chain acyl-rich (2, 3) and acetyl-rich (5, 6). The acetyl-rich paramylon acetate hexanoate (7), and 8 were prepared for comparison; 7 had DS values comparable to those of 5 and 6, whereas 8 and 9 had DS values comparable to those of 1a.

Table 1 also shows the molecular weights and DPs of the products. The $M_w$ and $M_m$ of the paramylon mixed esters ranged from $\sim 3.3 \times 10^5$ to $\sim 5.2 \times 10^5$ and from $\sim 2.3 \times 10^5$ to $\sim 4.3 \times 10^5$, respectively. The $M_w$ and $M_m$ of 8 were comparable to these values and those of 9 were 5–6 times larger than those of 1a. CAB used herein has lower molecular weights. The $M_w/M_m$ (i.e., polydispersity index) of the paramylon mixed esters ranged from 1.2 to 1.6, indicating that esterification did not significantly change the inherent near-monodispersity of paramylon (≈1.2). The $M_w/M_m$ of 8 was higher than those of the paramylon mixed esters because of the successive harsh extraction, purification, and fibrillation processes employed in the preparation of dissolving pulp (Savage et al., 1954), while the $M_w/M_m$ of 9 was comparable to those of the paramylon mixed esters. The DPs of the paramylon mixed esters ranged from ~840 to 1700, higher than those of the CAB used herein and the CABs used for previously reported melt spinning studies (Aranishi et al., 2006).

3.2. Thermal analyses

Prior to melt spinning, we examined the thermal properties ($T_m$, $T_d$, $T_p$, and MVR) of the solid polysaccharide mixed esters prepared by the ethanol precipitation method.

3.2.1. Melting point

Fig. 1a shows the DSC thermograms (first heating scan) of 1a–9. All the paramylon mixed esters exhibited $T_m$ values ranging from ~190 to 250 °C (Table 2). The thermograms of 1b–7 show only endothermic peaks. The thermogram of 1a differs from those of the other paramylon mixed esters in terms of the appearance of a distinct exothermic peak at 215.3 °C. Since exothermic peaks correspond to cold crystallization occurring during the heating process, cold crystallization is also thought to contribute partially to the endothermic peaks (Gan et al., 2017; Marubayashi et al., 2014; Mujica-García et al., 2016). Fig. 2 shows the WAXD diffractogram of the ethanol-precipitated solid of 1a. The appearance of some sharp diffraction peaks in the 20 range from ~10 to 25° and broad halos in the higher-angle region indicate the coexistence of crystalline and amorphous phases. The thermogram of 8 shows not only an endothermic peak but also an exothermic one at 173.7 °C, similar to that of 1a. The thermogram of 9 shows two endothermic peaks at 216.6 and 224.5 °C comparable to 1a. No exothermic peak appears despite structural similarities to 1a in terms of DS values.

3.2.2. $T_d$ and isothermal stability

$T_d$ is a typical index for evaluating resistance to heat degradation (Chen et al., 2010; Goto et al., 2000; Sato et al., 2014). Based on the $T_d$ of paramylon (~270 °C), the products can be categorized into three groups based on their $T_d$: (1) 1a–1c, 2, 3, 5–9 with $T_d$ values higher than that of paramylon; (2) 1d with $T_d$ comparable to that of paramylon; and (3) 4a and 4b with $T_d$ values lower than that of paramylon (Table 2). Hence, resistance to heat degradation apparently depends significantly on the chain length and DS of the acyl groups. $T_d$s of 8 and 9 are comparable to that of the structurally analogous 1a. Another index for heat resistance is isothermal stability; degradation of the solids is evaluated by continuously measuring the sample weight loss percentage upon heating at 246 ± 1.0 °C for 30 min. These incubation temperature and period are supposedly close to those required for the actual practical operation. The weight loss percentages indicate that all the polysaccharides, except for 1d, 4a, and 4b, show higher isothermal stabilities with weight loss less than 1.0% upon heating (Table 2). No significant difference in isothermal stability was observed between 1a and its analogues (8, 9).

For successful melt spinning, the extruding temperature must be lower than the decomposition temperature to avoid charring. In addition,
the wider the process window ranging from the melting temperature to the decomposition temperature, the easier is the melt spinning operation. Hence, we used the difference between $T_{d5}$ and $T_m$ (i.e., $T_{d5} - T_m$) as the evaluation index. As shown in Table 2, the $T_{d5} - T_m$ values are as large as 100 °C, except for 1c, 1d, 4a, and 4b.

### 3.2.3. Glass transition temperature

Fig. 1b shows the DSC curves (second heating scan) of 1a–9. Apparently, $T_g$ are confirmed for all the compounds. A comparison of the $T_g$ values of the paramylon acetate propionates (1a–1d) synthesized from acetic acid and propionic anhydride reveals that the higher the DSace (i.e., the lower the DSmc), the higher is the $T_g$ (Table 2). Since the polymer–polymer distance decreases with decreasing DSmc of the propionyl group, this trend seems reasonable. The $T_g$ values of the paramylon acetate propionates, prepared from propionic acid and acetic anhydride (4a and 4b, respectively), are higher than those of 1a–1c and are comparable to that of 1d. The higher $T_g$s of 1d, 4a, and 4b are due to their small polymer–polymer distances, as suggested by their higher DSace and lower DSmc than those of 1a–1c.

The similar DS values of 2 and 3 allow the effect of the chain length on $T_g$ to be explicitly examined. For instance, a single methylene elongation induces a reduction in $T_g$ as large as 14 °C. A comparison of the $T_g$s of 6 and 7, which have similar DS values, suggests that the longer the medium-chain acyl group, the lower is the $T_g$. The increase in chain length of the medium-chain acyl group from butyryl (5) to pentanoyl (6) is not responsible for the decrease in $T_g$; rather, this is probably ascribable to the stronger polymer–polymer interactions in 6 than those in 5, because the DSmc of 6 are larger and smaller, respectively, than those of 5. The $T_g$ values suggest that all the paramylon mixed esters can form melt-spun filaments with thermostability comparable to those of the petroleum-based amorphous polymers, including polystyrene and polycarbonate ($T_g$ = ~100 and ~139 °C, respectively), if they are successfully melt-spun (Claudy et al., 1983; Shamim et al., 2014).

The $T_g$ of 8 (136.4 °C) is ~16 °C higher than that of 1a, a structural analogue of 8 in terms of acyl chain length, DS, and molecular weight; this is attributable to the difference in glycosidic linkage ($\beta$-1,3 for 1a vs $\beta$-1,4 for 8). The compatibility of $T_g$s between 1a and 9 is reasonable because they are both $\beta$-1,3-glucan-based mixed esters with the same acyl group combination with close DS values.

#### 3.2.4. Exothermic phenomena

Fig. 1b shows that two exothermic peaks appear at 162.9 °C and 199.9 °C in the curve for 1a and one at 163.4 °C in that for 1b. Given that the exothermic peaks are due to cold crystallization (Gan et al., 2017;
Marubayashi et al., 2014; Mujica-Garcia et al., 2016), we think that 1a undergoes polymorph transition during heating from ambient temperature to ~200 °C, while 1b does not. The larger ΔHf values of 1a (3.85 and 4.91 J/g at 162.9 and 199.9 °C, respectively) than that of 1b (0.37 J/g) suggests that the former contains larger amorphous phase than the latter. This is because the crystallization rate of 1a is lower than the cooling rate (5.0 °C/min) and that of 1b is comparable to the cooling rate; therefore, a large part of 1a and 1b in the melt state turned to amorphous and crystalline phases, respectively, upon cooling to ambient temperature. Since 1a and 1b have comparable molecular weights, these differences in the thermograms are probably due to the differences in the acylation degrees; in other words, the differences in DSace and DSmc of only ~0.3 between 1a and 1b are large enough for inducing the differences in thermal behaviors. The degrees of acylation will be discussed in Section 3.7.

Thermograms of 1a and 1b show apparent endothermic peaks at 221.2 and 208.2 °C, respectively (Fig. 1b). One cannot say with conviction that melt-solidified 1a and 1b have high crystallinity based on the appearance of the large endothermic peaks alone, because cold recrystallization is a primary contributor to these peaks. Hence, we presume that both 1a and 1b can form crystalline filaments if successfully melt-spun, while the others cannot be spun. The thermogram of 8 shows a distinct endothermic peak at 234.4 °C, indicating that this compound is crystalline. No exothermic peak due to cold crystallization suggests that its crystallization was completed within the cooling process from 230 to 25 °C with a cooling rate of 5.0 °C/min during the first heating/cooling process. Thermogram of 9 shows broad and sharp exothermic peaks at 168.0 and 200.9 °C, respectively, and an endothermic peak at 222.4 °C. The similarity of thermogram profile between 1 and 9 suggests the similarity in their polymer packing in the solid state.

### 3.2.5. Melt volume flow rate

To determine whether the polysaccharide mixed esters are melt-spinnable using the custom-built melt spinning apparatus, we measured their MVRs using the melt indexer and weights employed for spinning, the results of which are listed in Table 3. We confirmed that 1a and 1b have higher MVRs and 1c and 1d have lower MVRs among the propionyl-rich paralymon acetate propionates. The difference is particularly pronounced when the paralymon mixed esters are subjected to extrusion using the 98.07-N weight at 240 °C. This is likely because 1a and 1b have longer polymer-polymer distances than 1c and 1d, as indicated by their lower DSmac and higher DSace values. Products 2 and 3 show higher MVR values than 1a and 1b due to the more pronounced thermoplasticization effect of the butanoyl and pentanoyl groups than that of the propionyl group. Compounds 4a and 4b are hardly extruded under the experimental conditions because of their high Tm above ~245 °C; the charred state of their filaments extruded at 250 °C is reasonable. This result suggests that the thermoplasticization effects of medium-chain acyl groups (butanoyl, pentanoyl, and hexanoyl) become apparent above a threshold temperature and force. Compound 8 shows lower MVR value than the structurally analogous 1a possibly due to the β-1,4-linkage in the main chain. Compound 9 was not extruded under the present experimental conditions due to its rather larger molecular weight than 1a (Table 1).

### 3.3. Melt spinnabilities

Prior to mechanical spinning, we examined the spinnabilities of all the compounds using manual spinning (spinning rate of ~50 cm/s) as a preliminary experiment using the custom-built melt spinning apparatus. Since the speed of manual spinning can be adjusted, facilitating a balance between the extruded volume of the melted solid and that of the spun filament for avoiding filament breakage, we consider this a useful means for evaluating the melt spinnability of filament materials than the mechanical spinning performed at a constant speed. The cylinder temperature and weight were set by reference to the Tm and MVR results to gain expected the MVR values of 10–100 cm³/10 min, which are roughly equivalent to or larger than the volumes of melt-spin filaments with a diameter of ~200 μm, e.g. cylinder temperature of 240 °C and 98.07-N weight for 1a. The manual spinning test confirmed that filaments longer than a few meters were produced from 1a and 1b; in contrast, only fragile and/or short filaments of length less than a dozen centimeters

Table 4
Preparation conditions and mechanical properties of monofilaments fabricated from 1a, 1b, and CAB.

| Run | Product | Cylinder temperature (°C) | Extruding force (N) | Spinning rate (rpm) | Maximum strength (cN/dtex) | Elongation at break (%) | Resistance (cN/dtex) | Young’s modulus (MPa) |
|-----|---------|---------------------------|--------------------|---------------------|-----------------------------|--------------------------|---------------------|----------------------|
| 1   | 1a      | 240                       | 98.07              | 80                  | 1.6 ± 0.7                   | 28.8 ± 4.7               | 10.7 ± 3.6          | 1386.4 ± 470.2       |
| 2   | 1a      | 240                       | 98.07              | 100                 | 2.8 ± 1.0                   | 28.2 ± 3.3               | 14.8 ± 7.5          | 1920.3 ± 968.8       |
| 3   | 1b      | 240                       | 98.07              | 110                 | 2.1 ± 0.9                   | 26.6 ± 4.2               | 12.4 ± 5.5          | 1615.6 ± 714.8       |
| 4   | 1b      | 245                       | 98.07              | 80                  | 2.2 ± 0.7                   | 27.1 ± 3.7               | 10.0 ± 2.3          | 1297.5 ± 304.7       |
| 5   | 1b      | 245                       | 98.07              | 100                 | 1.5 ± 0.3                   | 25.6 ± 2.6               | 10.2 ± 1.9          | 1266.3 ± 241.8       |
| 6   | CAB     | 165                       | 37.26              | _^                  | 0.5 ± 0.1                   | 5.6 ± 1.1                | 14.4 ± 1.7          | 1865.5 ± 225.2       |

* Manual spinning (~50 cm/s).
were obtained from 1c–3, 5–8 and no filaments were obtained from 4a, 4b, and 9, despite several attempts using different combinations of cylinder temperature, weight, and spinning rate. Hence, we chose 1a and 1b as the most promising filament materials among the paramylon mixed esters studied and subjected them to mechanical melt spinning.

Table 4 shows the spinning conditions used, i.e. the cylinder temperature, extruding force, and spinning rate. The cylinder temperature was set 15–20 °C higher than the Tm of the corresponding solid, enough for melting it inside the cylinder within 3 min. Since the cylinder temperature was ~100 °C lower than the Td5 value, polymer decomposition during the spinning process was negligible. Owing to mechanical limitations, the forces used herein for extrusion (98.07 N) were significantly lower than those employed for regular laboratory-scale melt spinning using a twin-screw microcompounder (4000–5000 N) (Hooshmand et al., 2014). The spinning rate, therefore, was decreased to 80–110 rpm (24–33 m/min), equivalent to the manual spinning rate; minor variation in spinning rate is needed to strike an optimum balance between the extruded volume of the melted solid and that of the spun filament, as attained in the manual spinning experiment.

We confirmed that under the spinning conditions listed in Table 4, long and fine monofilaments were produced from 1a and 1b (Fig. 3a and b). Fig. 4 shows the typical magnified SEM images of the melt-spun filaments.
filament surfaces, indicating that the filaments have uniform diameters, with no significant defects or roughness.

Table 4 also shows that the mechanical properties (maximum strength, elongation at break, and Young's modulus) of the spun monofilaments. There are no significant differences in the maximum strengths, resistances, and Young's moduli among the filaments spun from each product obtained at different spinning rates (Runs 1–3 for 1a and Runs 4 and 5 for 1b). Comparison between the 1a and 1b filaments reveals that the filaments spun from 1b have slightly lower maximum strength, resistance, and Young's modulus than those spun from 1a. Notably, since the properties of melt-spun filaments strictly depend on various spinning conditions, including shear rate of melted polymers, spinneret temperature, spinning rate, and cooling temperature, the mechanical properties listed in Table 3 do not weigh the relative merits of 1a and 1b as a filament material.

Solid 8 was unsuccessfully extruded using a cylinder temperature of 240 °C and a weight of 98.07 N, the same melt spinning conditions used for 1a (Table 4). Increasing the cylinder temperature from 240 to 250 °C enabled extrusion of 8 through the spinneret, but only brittle, charred, and short filaments were produced by manual spinning (Fig. 3c). These results indicate that 8 is less suitable for melt spinning than 1a, although 8 is a structural analogue of 1a. Instead, monofilaments spun from commercially available CAB were prepared by manual spinning, because mechanical spinning produced broken filaments due to the high spinning rate and tension. While the CAB is not a strict control because its molecular weight is 10 times lower than that of 1a and it has a different acyl group combination from 1a, comparison of the mechanical properties between the 1a/1b filaments and the CAB filaments indicates that filaments of 1a and 1b have mechanical properties comparable to those of the cellulose-based one obtained using melt spinning. Notably, the maximum strength of melt-spun filaments of 1a and 1b is comparable to that of cellulose acetate (CA) fibers (1.47–3.54 cN/dtex), spun from lyotropic crystals using the liquid crystal spinning method. This is useful for producing fibers with high breaking strength and high Young’s modulus (Kamidé, 2005), suggesting that the paramylon acetate propionate-based filaments can be put to practical use. We supposed that the high maximum strength stems from the crystalline nature of the filaments. Their crystallinity will be discussed in Section 3.5.

3.4. DSC analysis of monofilaments of paramylon acetate propionates

To gain further insight into the properties of the filaments melt-spun from 1a and 1b, we subjected them to DSC analysis. Fig. 5a shows the DSC profiles (first heating scan) of the filaments. The first heating scan of 1a, which is representative for examining the thermal properties of melt-spun filaments (Mujica-García et al., 2016), shows that two broad exothermic peaks with ΔH = 5.0 and 3.2 J/g, appearing at 153.5 and 207.0 °C, respectively, indicating that cold crystallization occurs in the filament as in the ethanol-precipitated and melt-solidified solids (Fig. 2). Two sharp exothermic peaks appear at 154.1 and 201.6 °C with ΔH of 9.0 and 5.6 J/g, respectively, during the second heating scan (Fig. 5b). The difference in exothermic peak width between the first and second heating scans is primarily attributable to the test sample form. In other words, roughly even heat-transfer distribution to the melt-solidified sample sealed in an aluminum pan induces cold recrystallization within a narrower temperature range to give sharp exothermic peaks (second scan), but cold recrystallization in the filamentary sample upon uneven heat-transfer distribution results in broader peaks (first scan). The differences in peak appearance can also be attributed to the lower crystallinity of the filament produced by quick cooling and higher crystallinity of the melt-solidified solid prepared by gradual cooling. The first and second heating scans of 1b show broad and sharp exothermic peak at 152.4 and 154.3 °C with ΔH of 7.5 and 8.5 J/g, respectively. The difference in exothermic peak width between the two peaks can be rationally accountable for by the same reasons as the 1a thermogram. Taken together, the DSC thermograms of the filaments indicate that the melt-spun filaments have crystalline character, albeit low in degree.

3.5. WAXD analysis of monofilaments of paramylon acetate propionates

DSC analysis indicated that the melt-spun filaments of 1a and 1b can have crystalline character. To examine this idea, they were subjected to WAXD analysis. Fig. 6 shows the diffractograms of the 1a and 1b filaments. A sharp peak in the low-angle region (i.e., at ~9°) and broad halos in the higher-angle region (i.e., >20°) in both diffractograms indicate the formation of the periodic structure of the paramylon backbone (Gan et al., 2017), suggesting that partial crystallization progresses during melt spinning. Based on the relative height of the sharp peaks at ~9°, crystallinity of the 1b filament is plausibly higher than that of 1a one. The solid 1b has higher melt velocity than 1a, suggested by a large difference in MVR values at the same temperature and weight as those used for each melt spinning process (i.e., 26.8 and 105.3 cm³/10 min for 1a and 1b, respectively). This allows 1b to gain higher polymer movement freedom and more time for recrystallization than 1a during the quenched solidification process. We also assumed that the higher degree of acetylation of 1b than that of 1a facilitates crystallization, as suggested by the lower ΔH values of the exothermic and endothermic peaks of the 1b thermogram (Fig. 1b). Although we do not seek for further reasons...
underlying the crystallinity difference, in this study, various spinning conditions cooperatively control the filament properties. Taken together, the WAXD and DSC results confirmed that both \textit{1a} and \textit{1b} can form crystalline filaments.

3.6. DMA analysis of monofilaments of paramylon acetate propionates

Fig. 7 shows representative curves for the storage modulus ($E'$), loss modulus ($E''$), and tan $\delta$ of the monofilaments spun from \textit{1a} (Run 1), \textit{1b} (Run 4), and CAB. The storage moduli of the filaments of \textit{1a} and \textit{1b} gradually decrease with increasing temperature up to $\sim$120 °C.

![Fig. 7](image)

Fig. 7. Dependence of viscoelastic parameters on temperature; (a) storage moduli, (b) loss moduli, and (c) tan $\delta$ of \textit{1a} (Run 1), \textit{1b} (Run 4), and CAB.
thereafter, the storage moduli decrease much steeply (Fig. 7a). Since their tan δ curves show maxima around 120 °C (Fig. 7c), the glassy states of 1a and 1b probably change to the rubber state around this temperature. Comparison between 1a and 1b reveals that a significant difference in storage modulus becomes pronounced above ~120 °C (Fig. 7a). The storage moduli at different temperatures are shown in Table 5. The storage modulus of 1b is ~1.5 times higher than that of 1a at 150 and 200 °C. Since the molecular weights of 1a and 1b were similar, this result suggested that the degree of polymer entanglement in the 1b filament is higher than that in the 1a filament. No significant difference in loss modulus between 1a and 1b was observed over the measurement temperature range (Fig. 7b). The loss modulus curves of 1a and 1b show maxima at ~120 °C, as observed in the tan δ ones. These temperatures are defined as T_g, as determined by DMA, and are comparable to the T_g values determined by DSC.

The storage modulus of CAB is comparable to those of 1a and 1b at temperatures below ~90 °C, and thereafter it becomes smaller than those of 1a and 1b, and the measurement was terminated at ~120 °C because of the sample break (Fig. 7a, Table 5). Since the T_g determined by DSC of CAB is 97.1 °C, comparable to the T_g determined based on its loss modulus and tan δ curves (Fig. 7b and c), this rapid drop in storage modulus of CAB is ascribable to the transition from glassy state to rubber state. The larger rapid descent in the storage modulus of CAB than those of 1a and 1b is probably due to the higher thermal vibration of the butanoyl group as compared to those of acetyl and propionyl groups and the lower molecular weights of CAB than those of n1a and 1b.

### 3.7. Chemical structures of the paramylon acetate propionates

As described above, 1a and 1b show differences in thermal behaviors, filament crystallinities, and mechanical properties at temperatures above T_g. Given the same acyl group combination and the close similarities of molecular weights between two compounds, the slight differences in acylation degree (~0.3) apparently induce these differences in physical properties. To gain insight into the chemical structural difference between them in terms of acyl substituents, acyl group distribution in the glucose unit was determined by quantitative 13C NMR spectroscopy.

| Product | Storage modulus (E’ (MPa)) |
|---------|-----------------------------|
|         | 50 °C | 100 °C | 150 °C | 200 °C |
| 1a      | 2660  | 1780  | 404   | 160    |
| 1b      | 2720  | 1860  | 614   | 245    |
| CAB     | 3090  | 952   | –     | –      |

Table 5. Storage modulus (E’) of monofilaments.

Fig. 8. Quantitative 13C NMR spectra of (a) 1a and (b) 1b; the insets show the corresponding magnified spectra in the range 168–174 ppm.
4. Conclusions

We examined the suitability of melt spinning for the preparation of monofilaments from paramylon mixed esters. We found that paramylon acetate propionates having DS_{ac} values of 0.5–0.7 and DS_{mc} values of 2.2–2.5 are melt-spinnable. Their monofilaments are mechanically tough, making them easy to handle, probably due to their high DPs (~1500) and their crystalline nature. In contrast, melt spinning of cellulose acetate propionate and curdul acetate propionate, structural analogues of the melt-spinnable paramylon acetate propionates, did not produce continuous filaments. Considering their unsuccessful melt spinning, the melt spinabilities of the paramylon acetate propionates are primarily explained based on their higher thermoplastics than these structural analogues. In addition, our process avoids the use of solvent and plasticizers. These results support our hypothesis that thermoplastic paramylon mixed esters can be transformed more readily into mechanically robust monofilaments than the structurally analogous cellulose and curdul derivatives, if their physical properties and spinning conditions are well-matched. Experiments for developing applications for these monofilaments are currently underway. Nonetheless, these paramylon-based monofilaments can be used in medical materials, such as sutures, because of their mechanical toughness, potential biodegradability, and biocompatibility.

5. Table 6

| Product | Partial DS_{ac} | Partial DS_{mc} |
|---------|----------------|----------------|
|         | C2            | C4            | C6         | C2            | C4            | C6         |
| 1a      | 0.11 (4)      | 0.20 (6)      | 0.15 (5)   | 0.89 (30)     | 0.72 (24)     | 0.93 (31)   |
| 1b      | 0.23 (8)      | 0.28 (9)      | 0.21 (7)   | 0.75 (25)     | 0.62 (21)     | 0.87 (30)   |

Values in parentheses indicate the percentage of substituent occupancy in a glucose residue.

6. Declarations

Author contribution statement

Motonari Shibakami: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Mitsugu Sohma, Norihiro Kijima: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Tadashi Nemoto: Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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