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Syntheses of glucomannan esters and their thermal and mechanical properties

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ABSTRACT

Fully substituted glucomannan (GM) acylates with acyl carbon numbers (n) of 2, 3, 4, 5, 6, 8, 10, and 12 were prepared from konjac GM (KGM) in carboxylic acid/trifluoroacetic anhydride (TFAA). GM acetate acylates (n = 3, 4, 5, 8, 12, 16, and 18) were prepared from KGM in acetic acid/carboxylic acid/TFAA. Differential scanning calorimetry (DSC) and X-ray diffraction revealed that the GM esters did not exhibit melting peaks and reflections derived from crystal, indicating they were amorphous. The glass-transition temperatures (T_gs) of the GM esters tended to decrease with increasing acyl carbon number, ranging from 174 °C for GM acetate (GMAc) to 64 °C for GM laurate (GMLa). Colorless and transparent GM ester films were obtained by solvent casting and thermo-pressing. The mechanical properties of the GM ester films were controlled by the acyl group structure.

1. Introduction

Konjac glucomannan (KGM) is the one of the polysaccharides isolated from the tubers of *Amorphophallus konjac* plants. KGM consists of β-1,4-linked D-glucose and D-mannose residues as the main chain, with branches joined through the C3 carbon of glucosyl or mannosyl residues (Kato & Matsuda, 1969; Maeda, Shimahara, & Sugiyama, 1980; Smith & Srivastava, 1959). The molecular ratio of glucose to mannose has been reported to be ca. 1.6, and its composition is dependent on its origin (Kato & Matsuda, 1969; Maeda et al., 1980; Smith & Srivastava, 1959). Katsuraya et al. (2003) have proposed that one branching position is the C6 position of the glucosyl unit.

KGM has a high molecular weight (more than 1 000 000 Da), is water soluble, forms gels readily, and is biodegradable and biocompatible. Because of its valuable characteristics, KGM has been studied extensively in many fields, such as food and food additives, films, coating materials, cosmetics, drug delivery, and biomedical science (Yu, Huang, & Xiao, 2006; Zhang, Xie, & Gan, 2005).

Polysaccharides, such as cellulose, hemicellulose, chitin, and starch, are regarded as important renewable materials from natural resources. It is well known that polysaccharides do not exhibit thermoplastic properties, because of their strong inter- and intra-molecular hydrogen-bonding. In the case of cellulose, thermoplastic materials have been prepared by esterification, and the obtained cellulose esters, such as cellulose acetate and propionate, are widely used in industry (Edgar et al., 2001). Despite the substantial literature on preparation of alkyl esters of cellulose (Crepy, Miri, Joly, Martin, & Lefebvre, 2011; Morooka, Norimoto, Yamada, & Shiraishi, 1984; Sealey, Samaranayake, Todd, & Glasser, 1996), starch (Sagar & Merrill, 1995; Yang & Montgomery, 2006), chitin (Ma, Yang, Kennedy, & Nie, 2009; Teramoto, Miyata, & Nishio, 2006; Zong, Kimura, Takahashi, & Yamane, 2000), and xylan (Fundador, Enomoto-Rogers, Takemura, & Iwata, 2012a; Fundador, Enomoto-Rogers, Takemura, & Iwata, 2012b; Sun, Fang, & Tomkinson, 2000), there have been a few studies of glucomannan (GM) esters or their applications as plastic materials (Chen, Zong, & Li, 2006; Koroskenyi & McCarthy, 2001; Tian, Dong, & Chen, 1998). In most studies, the degrees of substitution (DS) of GM derivatives are low and insufficient to show plastic properties. This is probably because of their low solubilities, and gel formation by KGM in organic solvents, resulting in low reactivity. The films or membranes composed of KGM reported so far have been mostly unmodified materials or blends with other polymers (Fan, Zheng, Xu, Huang, & Zhang, 2007; Xiao, Lu, & Zhang, 2001; Xu, Luo, Lin, Zhuo, & Liang, 2009). Highly substituted KGM esters, as well as cellulose esters, are promising candidates for bio-based thermoplastic materials in industry.

Carboxylic acid/trifluoroacetic anhydride (TFAA) mixed systems are efficient systems for cellulose esterification (Bourne, Stacey, Tatlow, & Tedder, 1949; Tsuzuki, Shiraishi, & Yokota, 1980). We recently succeeded in preparing fully substituted GM acetate (GMAc), using acetic acid and TFAA, with the aim of preparing thermoplastic materials from KGM (Enomoto-Rogers, Ohmomo, & Iwata, 2013). The GMAc formed amorphous films with high

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mechanical properties. It was expected that GM acylates with longer alkyl chains would also be plastic materials, and that their properties could be controlled by the substituent structure. In the present study, we have prepared fully substituted GM acyl homoesters and mixed esters in carboxylic acid/TFAA mixed systems. The carbon numbers of the acyl groups were varied from 2 to 18 to investigate their structure–property relationships. Film preparation, and the thermal and mechanical properties of the obtained GM esters and their correlations with the structures of substituents, were investigated.

2. Experimental

2.1. Materials

KGM (Proporl® A) was kindly provided by Shimizu Chemical, Co. (Hiroshima, Japan). TFAA and all other reagents were commercially obtained and used without further purification.

2.2. Preparation of GM homoesters

GM acylates, which are substituted with one type of acyl group, are termed GM homoesters. GM homoesters were prepared according to the preparation procedure for GMAc described in our previous study (Enomoto-Rogers et al., 2013). The acyl carbon number (n) was varied from 2 to 12. A representative procedure, for GM propionate synthesis, is as follows. KGM (0.5 g) was dissolved in water (100 ml) and freeze-dried. A premixed solution of TFAA (20 ml) and propionic acid (20 ml), which had been stirred at 50 °C for 20 min, was immediately added to the freeze-dried GM in a flask. The solution was stirred at 50 °C for 1.0 h under nitrogen. After cooling to room temperature, the solution was poured into ethanol (1.0 l). The precipitate was filtered, washed with ethanol, dissolved in chloroform, and reprecipitated in ethanol, before finally being filtered, washed with ethanol, and dried in vacuo to give a solid compound, GM propionate (GMPr, n = 3; 0.75 g, 73%). For other GM homoesters, appropriate carboxylic acids (20 ml or 20 g; n = 2–12) were used instead of propionic acid. The yields (%) of the obtained GM homoesters were as follows: GMAc (n = 2; 0.76 g, 85%), GM butyrate (GMBu, n = 4; 0.78 g, 66%), GM valerate (GMVa, n = 5; 0.88 g, 67%), GM hexanoate (GMHe, n = 6; 0.85 g, 60%), GM octanoate (GMOc, n = 8; 1.24 g, 74%), GM decanoate (GMDe, n = 10; 1.56 g, 81%) and GM laurate (GMLa, n = 12; 1.41 g, 73%). The reaction time for GMLa was set at 2.0 h. GM homoesters with carboxylic acids with longer chains, such as palmitic acid (n = 16) and stearic acid (n = 18), could not be obtained because of the low solubility of KGM in these acid/TFAA systems. The number-average degree of polymerization (DP_n) was calculated by dividing the number-average molecular weight (M_n) of the GM ester by the molecular weight of a triacylated anhydro glucose or mannose unit, as listed in Table 1. The DS of the acyl group was calculated from the ratio of the integrated area of the methyl protons of the acyl group to that of the ring protons of glucose and mannose, as follows: DS = ([CH_3]/3)/([ring-H]/7). The peaks in the ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of GMAc were assigned in detail in a previous study (Enomoto-Rogers et al., 2013).

2.3. Preparation of GM mixed esters

GMAc acylate mixed esters, which are substituted with acetyl and acyl (n = 3–18) groups, are termed GM mixed esters. A representative procedure, for the synthesis of GMAc palmitate (GMAcPa, n = 2, 16) is as follows. KGM was pretreated with water, ethanol, and hot acetic acid. GM (0.5 g) was dissolved in water (100 ml); the solution was poured into ethanol (500 ml), and the precipitated GM was collected by filtration. The precipitated GM was dispersed in acetic acid (20 ml) and heated at 110 °C with vigorous stirring to remove residual water and ethanol by evaporation. After 1 h, the GM was filtered to remove excess acetic acid. The GM, which is "wet" in acetic acid, was used as the starting material for esterification. The obtained GM (0.5 g) was added to a premixed solution of TFAA (20 ml) and palmitic acid (20 ml), which was stirred at 50 °C for 20 min. The mixture was stirred at 50 °C for 30 min under nitrogen. The reaction solution was poured into methanol, filtered, and dried in vacuo to give a solid compound, GMAcPa (1.24 g, 77% yield).

Carboxylic acids (20 ml or 20 g), namely propionic acid, butyric acid, valeric acid, lauric acid, palmitic acid, and stearic acid, were used instead of palmitic acid to obtain the corresponding GM mixed esters. The yields (%) of the esters were as follows: GM acetate propionate (GMAcPr, n = 2, 3; 0.62 g, 64%), GM acetate butyrate (GMAcBu, n = 2, 4; 0.19 g, 74%), GM acetate valerate (GMAcVa, n = 2, 6; 0.29 g, 77%), GM acetate laurate (GMAcLa, n = 2, 12; 1.19 g, 77%), and GM acetate stearate (GMAcSt n = 2, 18; 1.81 g, quantitative). The DS values of the acetyl and acyl groups were calculated from the ratio of the integrated area of the methyl protons of the acetyl group, as follows: $DS(Ac) = 3 \times [CH_3(Ac)]/([CH_3(acyl)] + [CH_3(Ac)])$, $DS(acyl) = 3 \times [CH_3(acyl)]/([CH_3(acyl)] + [CH_3(Ac)])$. The average molecular weight of one esterified anhydro sugar unit was calculated as follows: M(esterified anhydro sugar unit) = M(anhydro sugar unit) + $DS(Ac) \times (M(Ac) - 1) + DS(acyl) \times (M(acyl) - 1)$; M(acyl): molecular weight of acyl group, M(anhydro sugar unit) = 162.16. The DP_n values of the GM mixed esters were calculated by dividing the M_n by the average molecular weight of the esterified anhydro sugar unit.

2.4. Nuclear magnetic resonance (NMR) measurements

^{1}H NMR spectra were recorded with a JEOL JNM-A500 FT-NMR (500 MHz) spectrometer, using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and coupling constants (J) were reported in ppm and Hz, respectively.

2.5. Gel permeation chromatography (GPC) measurements

Number- and weight-average molecular weights (M_n and M_w) and polydispersity index values (M_w/M_n) were estimated by GPC (CBM-20A, DGU-20A_3, LC-6AD, SIL-20AC_{HT}, CTO-20A, RID-10A, Shimadzu) in chloroform at 40 °C. Shodex columns (K-806 M, K-802) were used, and the flow rate was 0.8 ml/min. A calibration curve was obtained using polystyrene (PS) standards (Shodex).

2.6. Thermogravimetric (TGA) analysis

TGA was carried out using a Thermo Plus TG 8120 (Rigaku) instrument under a nitrogen atmosphere. Thermograms were acquired between 30 and 450 °C at a heating rate of 20 °C/min.

2.7. Differential scanning calorimetry (DSC) measurements

DSC thermograms were recorded using a DSC 8500 (Perkin-Elmer) under a nitrogen atmosphere. The samples were first heated from 25 to 250 °C (first heating scan) at 100 °C/min, and then immediately quenched to −70 °C. The second heating scan was run from −70 to 350 °C at a heating rate of 100 °C/min. The glass-transition temperature (T_g) was recorded as the midpoint temperature of the heat capacity transition in the second heating scan.

2.8. Wide-angle X-ray diffraction analysis

Wide-angle X-ray patterns were obtained using a Rigaku RINT 2000 system operated at 40 kV and 200 mA. Measurements were performed using a Bragg-Bretano-type $2\theta/\theta$ goniometer in

Table 1
Characteristics of GM esters.

Glucomannan esters		Acyl carbon number (n)	M_n (10^{-5})[a]	M_w (10^{-5})[a]	M_w/M_n[a]	DS (Ac)[b]	DS (acyl)[b]	M (Ac)[c]	M (acyl)[c]	Average molecular weight of anhydro sugar unit[d]	DP_n (10^3)[e]	T_g (°C)
Homoesters												
Glucomannan acetate	GMAc	2	3.0	5.6	1.9	–	3.0	–	43	288	1.03	174
Glucomannan propionate	GMPr	3	8.5	15.0	1.9	–	3.0	–	57	331	2.56	135
Glucomannan butyrate	GMBu	4	5.9	11.2	1.9	–	3.0	–	71	373	1.58	99
Glucomannan valerate	GMVa	5	6.3	11.8	1.9	–	3.0	–	85	415	1.53	71
Glucomannan hexanoate	GMHe	6	8.9	16.2	1.8	–	3.0	–	99	458	1.94	61
Glucomannan ontanoate	GMOc	8	9.4	18.6	2.0	–	3.0	–	127	542	1.73	59
Glucomannan decanoate	GMDe	10	10.9	21.4	2.0	–	3.0	–	155	625	1.74	67
Glucomannan laurate	GMLa	12	6.4	16.7	1.8	–	3.0	–	183	709	0.90	64
Mixed esters												
Glucomannan acetate propionate	GMAcPr	2, 3	0.4	0.7	1.6	0.8	2.2	57	57	330	0.12	138
Glucomannan acetate butyrate	GMAcBu	2, 4	1.2	2.1	1.7	0.9	2.1	57	71	360	0.33	126
Glucomannan acetate valerate	GMAcVa	2, 5	1.0	1.5	1.6	1.0	2.0	57	85	387	0.25	109
Glucomannan acetate laurate	GMAcLa	2, 12	0.7	1.1	1.7	1.2	1.8	57	183	560	0.12	70
Glucomannan acetate palmitate	GMAcPa	2, 16	0.6	1.3	2.3	1.7	1.3	57	239	568	0.10	86
Glucomannan acetate stearate	GMAcSt	2, 18	0.9	2.6	2.9	2.3	0.7	57	267	478	0.19	97

[a] Estimated by GPC using polystyrene standards.
[b] Calculated from the peak areas of methyl protons of acyl and acetyl groups in ^{1}H NMR spectra.
[c] Molecular weight of acetyl and acyl groups.
[d] Calculated from DS values of acetyl and acyl groups, as follows: M(esterified anhydro sugar unit) = M(anhydro sugar unit) + DS(Ac) × (M(Ac) − 1) + DS(acyl) × (M(acyl) − 1), M(anhydro sugar unit of glucose or mannose) = 162.16.
[e] Caluculated from M_n and an average molecular weight of anhydro glucose or mannose unit.

reflection mode. Ni-filtered Cu-Kα radiation (λ = 0.15418 nm) was collimated in a 1/2-degree divergence slit, 1/6-degree scatter slit, and 0.15-mm receiving slit. Scans were performed twice in the 2θ range 2–40°, with a scan rate of 0.5°/min and a step size of 0.1°.

2.9. Preparation of solvent-cast films

The GM esters (0.4 g) were dissolved in chloroform (10 ml) and poured onto plates (diameter 4 cm). The solvent was then evaporated in air at room temperature.

2.10. Preparation of thermo-pressed films

GM homoester samples (0.5 g) were placed between stainless-steel sheets and pressed at 250 °C for GMAc, 200 °C for GMPr, and 150 °C for other GM esters for 2 min. The film thickness was controlled by varying the pressure from 1 MPa to 30 MPa.

2.11. Dynamic mechanical analysis (DMA)

DMA measurements were performed with a DVA-200S analyzer (IT Measurement Control, Osaka, Japan). Temperature scans at a frequency of 1 Hz were carried out in the range −150 to 300 °C at a heating rate of 5 °C/min under a nitrogen atmosphere. The specimens (18 mm × 5 mm) were prepared from thermo-pressed film.

2.12. Tensile tests

Tensile tests were carried out on the GM ester films at room temperature using an EZ-test machine (Shimadzu, Japan). The crosshead speed was 20 mm/min, and the initial gauge length was 10 mm. Five specimens (30 mm × 2 mm) were used for each measurement, and the data were averaged for each film.

3. Results and discussion

3.1. Preparation of GM homoesters

In a recent study, we successfully prepared fully substituted GMAc from KGM in an acetic acid/TFAA mixed system (Enomoto-Rogers et al., 2013). KGM was pretreated by dissolving in water and then freeze-drying. It was necessary to allow easy access of the reagents to the GM molecules to achieve efficient esterification. In the present work, this method was applied to other carboxylic acids with acyl carbon numbers n = 3–12. The freeze-dried KGM dissolved easily in these carboxylic acid/TFAA mixed solutions. Dissolution of KGM in the solution and esterification were generally achieved within 1.0–2.0 h. When GM was treated with a palmitic acid (n = 16)/TFAA or stearic acid (n = 18)/TFAA mixed system to obtain GM esters with longer alkyl chains, GM was poorly soluble in these systems. The viscosity of the system increased, resulting in formation of a cloudy, swollen product.

Representative ^{1}H NMR spectra of GMPr (n = 3) and GMLa (n = 12) are shown in Fig. 1. The peaks were assigned according to the assignments for GMAc reported in the previous study (Enomoto-Rogers et al., 2013). The NMR measurements revealed that the DS values were 3.0 for all the samples, and that fully substituted GM homoesters were successfully obtained. The molecular weights of the GM esters were determined by GPC, and their characteristics are listed in Table 1. The DP_n was calculated by dividing the M_n of the GM ester by the molecular weight of a triacylated anhydro glucose and mannose unit.

3.2. Preparation of GM mixed esters

To introduce longer acyl groups into the GM chain, such as palmitoyl (n = 16) or stearoyl (n = 18) groups, esterification of GM using a mixture of acetic acid and palmitic or stearic acid was investigated. When freeze-dried GM was dissolved in acetic

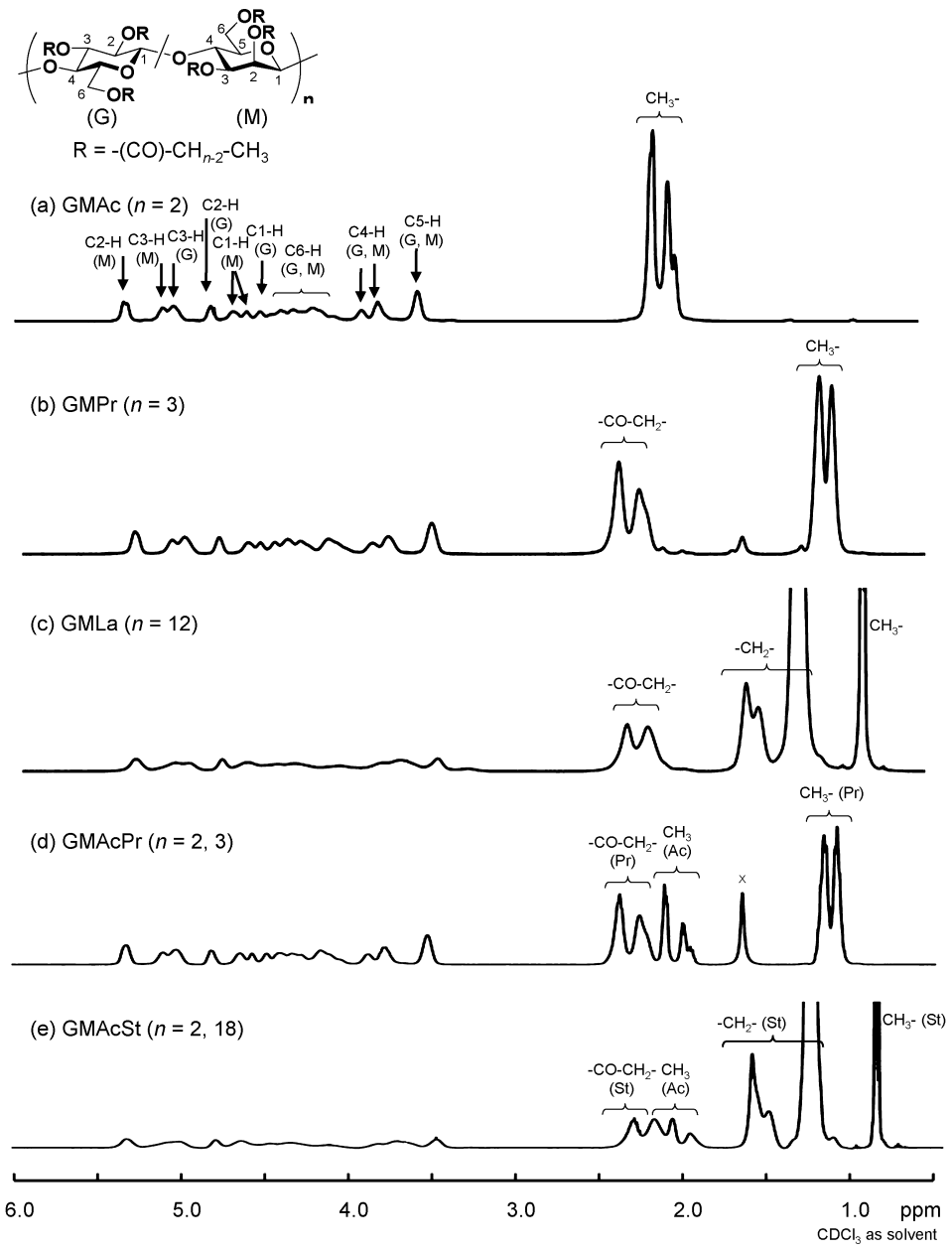

Fig. 1. ^{1}H NMR spectra of (a) GMAc, (b) GMPr, (c) GMLa, (d) GMAcPr, and (e) GMAcSt; G: glucose, M: mannose.

acid/palmitic or stearic acid/TFAA mixed systems, according to the method described in the previous section, the GM was esterified mainly by acetic acid, probably because its reactivity is higher than these fatty acids. When the ratio of acetic acid in the mixed acid system was low, the GM hardly dissolved and formed a cloudy, swollen product. Yang et al. reported that efficient acylation of starch was achieved after prior heating in acetic acid (Yang & Montgomery, 2006). In this work, therefore, GM granules were dissolved in water as a pretreatment; the solution was poured into ethanol, and then the precipitated GM was collected by filtration. The precipitated GM was dispersed in acetic acid and heated at 110 °C, with vigorous stirring, to remove residual water and ethanol by evaporation. It was difficult to replace the water and ethanol by washing with acetic acid at room temperature, as a result of swelling. After removal of water and ethanol, the GM was filtered to remove excess acetic acid. The GM, which is "wet", in acetic acid was loaded into the carboxylic acid/TFAA mixed solution, and the GM was esterified in the acetic acid/carboxylic acid/TFAA mixed system.

GM acetic-fatty acid mixed esters, i.e., GMAcPa (n = 2, 16) and GMAcSt (n = 2, 18), were successfully obtained by this method. In the same manner, other GM mixed esters, i.e., GMAcPr (n = 2, 3), GMAcBu (n = 2, 4), GMAcVa (n = 2, 6), and GMAcLa (n = 2, 12), were also obtained for comparison with the corresponding GM homoesters. Representative ^{1}H NMR spectra of GMAcPr and GMAcSt are shown in Fig. 2d and e. The total DS values of the acetyl and acyl groups were calculated as 3.0 for all the samples, indicating quantitative substitution of the three hydroxyl groups of GM. The DS value of the acyl group decreased with increasing number of acyl carbons, probably as a result of stearic hindrance caused by long and bulky alkyl chains. The M_n and M_w values of the GM esters were determined by GPC, and their characteristics are listed in Table 1. The M_n and DP_n

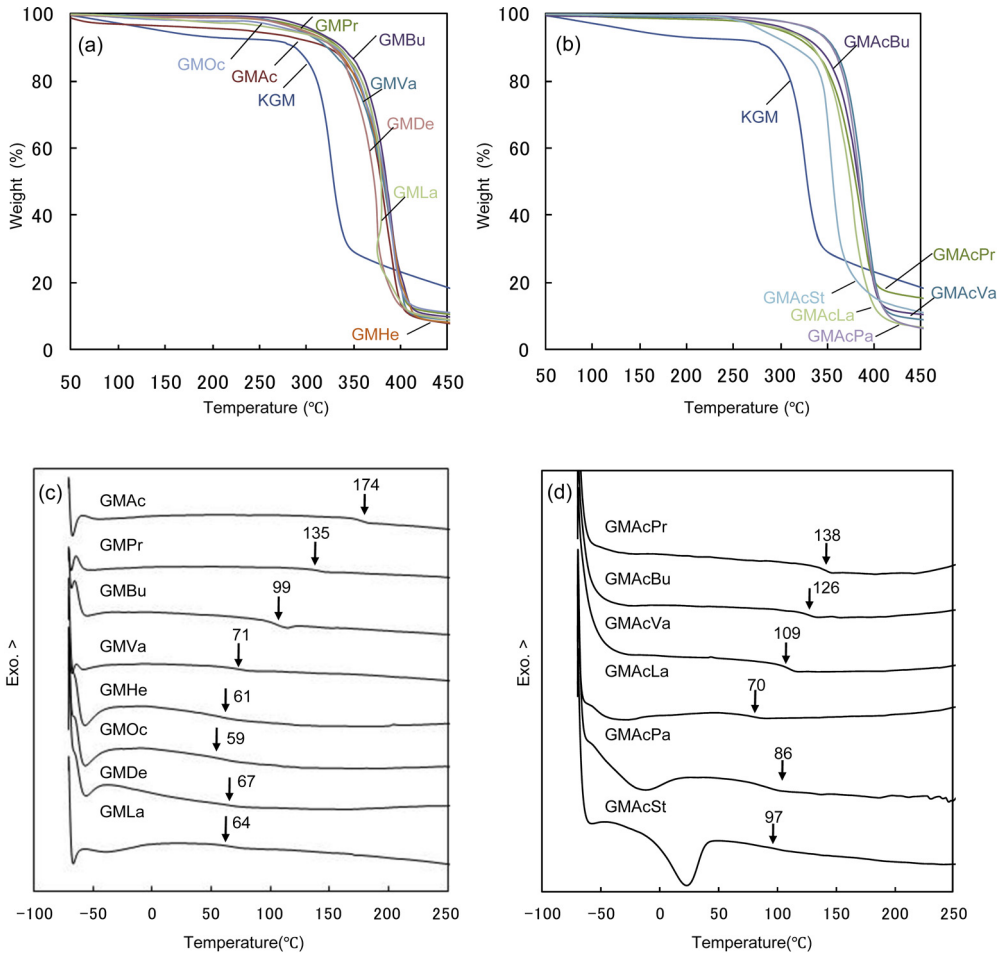

Fig. 2. (a), (b) TGA and (c), (d) DSC thermograms of the GM acylates (left) and the GM acetate acylates (right).

values of the GM mixed esters were lower than those of the corresponding homoesters. It is likely that the GM chain was hydrolyzed when it was heated in acetic acid during pretreatment.

3.3. Thermal properties of GM esters

The thermal behaviors of the GM esters were analyzed using TGA and DSC. The TGA thermograms are shown in Fig. 2a and b. The decomposition temperatures at 50% weight loss for the GM esters were ca. 372–385 °C. These values were higher than that of KGM (329 °C); the thermal stability of KGM was improved by acylation. The decomposition temperatures were independent of the acyl carbon number.

Fig. 3b and c shows the second heating cycles of the DSC thermograms of the GM esters. The heating rate was set at 100 °C/min, because no peak was observed at the usual heating rate of 10 °C/min. This suggests that molecular motion of the chains in the glass state of the GM esters is quite restricted. The GM esters showed no melting point, indicating that they were amorphous.

All the GM esters showed a peak attributable to a T_g. The T_gs of the GM homoesters tended to decrease with increasing acyl carbon number, and ranged from 174 °C for GMAc to 64 °C for GMLa. The T_gs of GMAc and GMPr were higher than those reported for other oil-based amorphous polymers, such as PS (ca. 100 °C) and poly(methyl methacrylate) (ca. 106 °C), and comparable with that of cellulose triacetate (ca. 180 °C) (Billmeyer, 1984; Mark, 1996). The GM mixed esters exhibited T_gs that tended to be higher than those of the corresponding homoesters. The observed T_gs were between those of acetates and acylates, showing that the acetyl groups contributed to increasing the T_gs. This suggested that the thermal properties of GM esters could be controlled by the structure and DS of the acyl groups.

3.4. Preparation of solvent-cast films and thermo-pressed films of GM esters

All the GM esters were insoluble in water and ethanol, and soluble in organic solvents, such as ethyl acetate, THF, and chloroform. Colorless and transparent self-standing films of GM esters were obtained by solvent casting from chloroform solution. Fig. 3a shows representative images of solvent-cast films of GMPr, GMBu, and GMLa. The preparation of thermo-pressed films of GM esters was also investigated by heating at temperatures above their T_gs; colorless and transparent self-standing films were successfully obtained. Fig. 3b shows representative images of thermo-pressed films of GMPr, GMBu, and GMLa. As can be seen in the images, GMPr and GMBu formed hard films and GMLa formed a soft film. Their mechanical properties are discussed in the following section. These results suggest that thermo-pressing is an efficient method for preparing injected materials from GM esters.

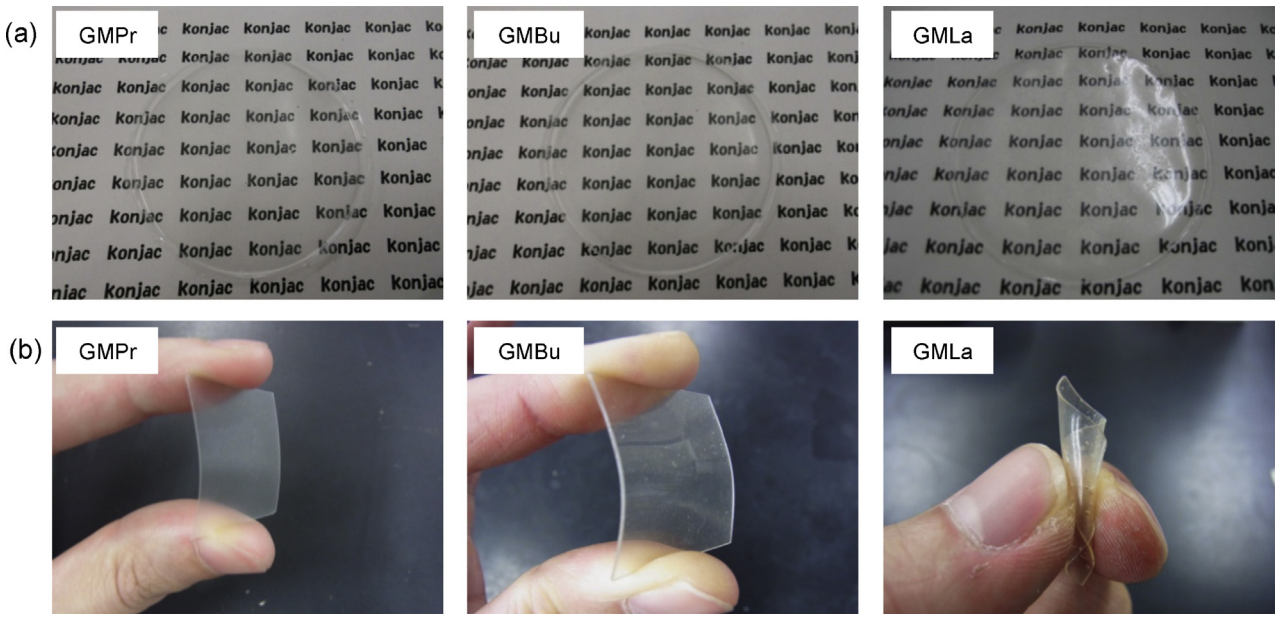

Fig. 3. Representative images of (a) solvent-cast films and (b) thermo-pressed films of GMPr, GMBu, and GMLa.

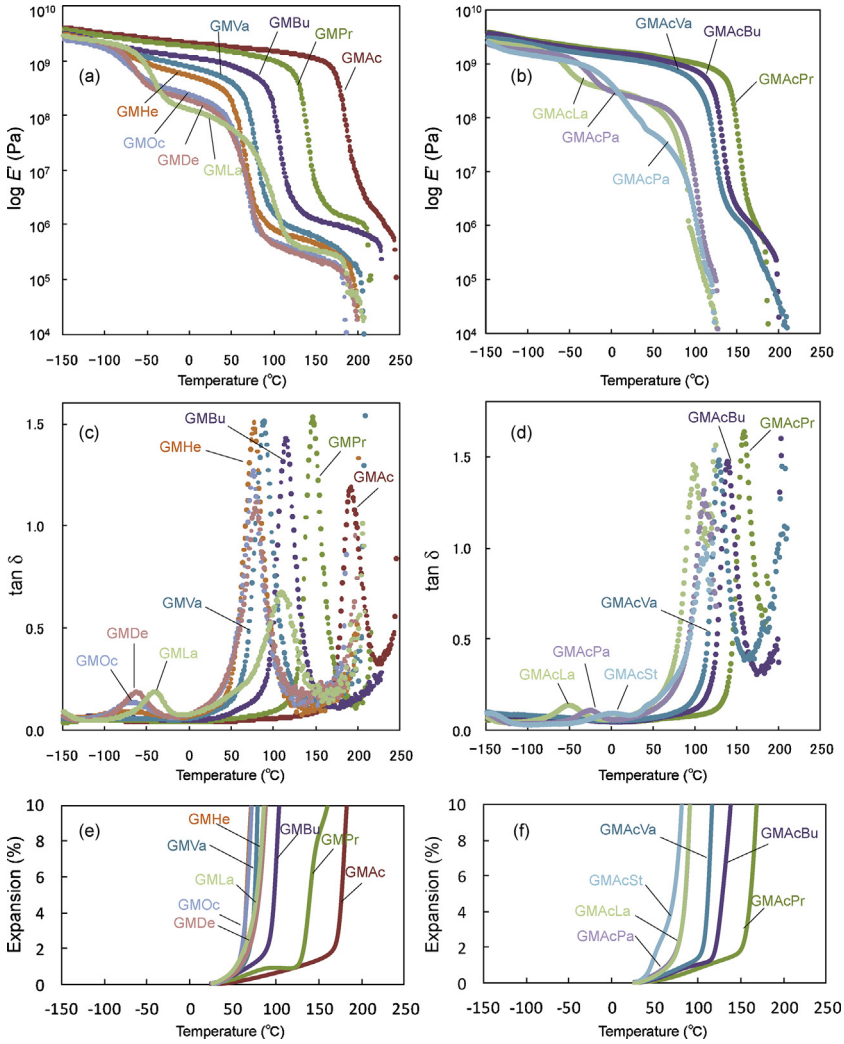

Fig. 4. (a), (b) Plots of storage modulus (E'); (c), (d) loss tangent ($\tan\delta$); and (e), (f) thermal expansion curves of thermo-pressed films of GM homoesters (left) and GM mixed esters (right).

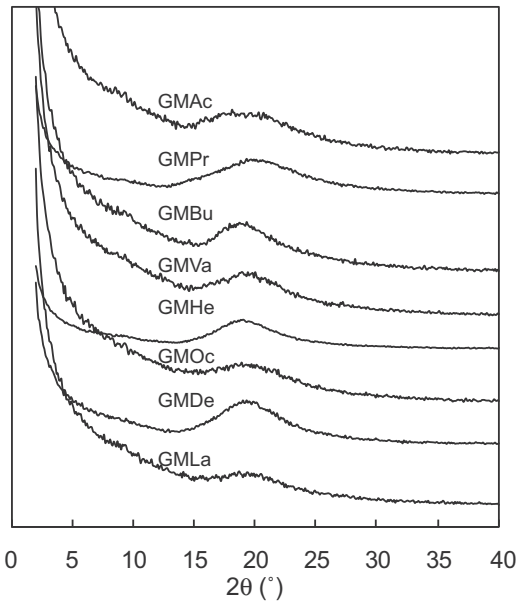

Fig. 5. X-ray diffractograms of GM homoesters.

3.5. DMA of GM ester films

DMA was carried out using thermo-pressed films of GM esters. For all the GM esters, the storage modulus (E') showed a marked drop, accompanying a loss tangent (tanδ) peak at the temperature corresponding to the T_g, as shown in Fig. 4. The T_gs obtained by DMA at 5 °C/min were not substantially different from those obtained by DSC thermograms in Fig. 2, supporting that DSC thermograms scanned at 100 °C/min were reliable.

In the case of GM esters with acyl carbon numbers greater than 6, E' showed a small drop, accompanied by a pronounced tanδ peak. The modulus drop and tanδ peak were more pronounced for esters with longer alkyl chains. The same phenomenon has been observed for cellulose fatty acid esters (Crepy et al., 2011; Morooka et al., 1984; Sealey et al., 1996; Vaca-Garcia, Gozzelino, Glasser, & Borredon, 2003). The observed modulus drop and tanδ peak were attributed to a relaxation of alkyl side-chains.

3.6. X-ray diffraction measurements

The X-ray diffraction patterns of GM esters are shown in Fig. 5. No specific diffraction peak derived from crystals was observed, and only broad peak were observed at 2θ = ca. 20°, which is characteristic of non-crystalline materials. This result is in good agreement with the fact that GM esters had no T_m, indicating that GM esters were amorphous. According to the study on cellulose acylates (n = 8–18) (Crepy et al., 2011), the peak top position at 2θ = ca. 20° shifted to higher angle with increasing alkyl chain length from 2θ = 20° to 22° (n = 8–18). In the case of cellulose stearate (n = 18), they suggested that the peak at 2θ = ca. 20° was consisting of two overlapping peaks due to amorphous (2θ = 19.8°) and crystalline of alkyl side-chains in α-hexagonal lattice (2θ = 21.2°). However, in the X-ray diffractograms of GM homoesters, broad peaks at 2θ = ca. 20° showed no substantial peak shift depending on alkyl chain length, supporting that the alkyl side-chains of GM esters were not crystallized.

The X-ray diffraction patterns of alkyl esters of cellulose (Crepy et al., 2011; Morooka et al., 1984; Sealey et al., 1996), chitin (Teramoto et al., 2006) or xylan (Fundador et al., 2012b), showed the diffraction at the low-angle region (2θ = 2–7°), which is attributed to the periodic layered structure of the main-chain formed by side-chain packing. In the case of GM esters, no peak was observed within the same region 2θ = 2–7°. This is suggesting that there was no specific packing of alkyl side-chains or periodic structure in GM main-chain. It is likely because GM is consisting of glucose and mannose unit in random sequence and that highly-ordered structure was hardly formed.

Table 2
Mechanical properties of GM esters.

GM esters	Breaking strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
Solvent-cast film			
GMAc	41 ± 4	27 ± 7	0.69 ± 0.06
GMPr	40 ± 6	35 ± 14	0.69 ± 0.05
GMBu	33 ± 6	83 ± 26	0.45 ± 0.06
GMVa	23 ± 4	160 ± 39	0.27 ± 0.02
GMHe	18 ± 2	149 ± 11	0.20 ± 0.02
GMOc	14 ± 2	300 ± 25	0.09 ± 0.01
GMDe	10 ± 1	268 ± 19	0.07 ± 0.01
GMLa	11 ± 2	426 ± 90	0.05 ± 0.01
Solvent-cast film			
GMAcPr	32 ± 3	40 ± 14	0.33 ± 0.05
GMAcBu	33 ± 3	51 ± 21	0.43 ± 0.07
GMAcVa	26 ± 4	53 ± 27	0.42 ± 0.02
GMAcHe	9.6 ± 1.6	179 ± 62	0.12 ± 0.01
GMAcPa	9.4 ± 1.3	101 ± 25	0.22 ± 0.02
GMAcSt	8.2 ± 1.5	108 ± 44	0.09 ± 0.01
Thermo-pressed film			
GMPr	52 ± 9	133 ± 16	1.06 ± 0.24
GMBu	53 ± 10	66 ± 16	0.58 ± 0.06
GMVa	28 ± 5	225 ± 20	0.23 ± 0.06
GMHe	19 ± 4	329 ± 81	0.15 ± 0.07
GMOc	10 ± 0.8	107 ± 32	0.12 ± 0.03
GMDe	10 ± 1.5	257 ± 27	0.09 ± 0.01
GMLa	4.8 ± 0.4	64 ± 21	0.05 ± 0.01

3.7. Mechanical properties of GM ester films

Tensile tests were carried out on the GM ester films, and the results are listed in Fig. 6 and Table 2. As shown by the strain–stress curves of the GM homoester cast-films in Fig. 6a, the tensile strength and Young's modulus tended to decrease with increasing acyl carbon number. The elongation at break of the esters increased with increasing acyl carbon number. The highest tensile strength values were observed with GM homoesters with short alkyl chains. The tensile strengths of GMAc and GMPr were 40 and 44 MPa, respectively, which were comparable with those of PS (30–60 MPa). GMLa showed the highest elongation at break value (426%) and the lowest tensile strength (3.1 MPa). These trends and values of the mechanical properties were similar to those of cellulose esters (Crepy et al., 2011; Joly, Granet, Branland, Verneuil, & Krausz, 2005). The GM mixed esters showed the same trends in their tensile properties as the GM homoesters, as shown in Fig. 6b. GMAcLa, GMAcPa, and GMAcSt showed lower elongations at break compared with GMLa, probably because of the low DS value of the acyl group. It seemed that the acetyl group contributed to their lower elongation at break values. Fig. 6c shows strain–stress curves of the thermo-pressed films of GM homoesters (n = 3–12). The tensile strengths of GMPr and GMBu were 52 and 53 MPa, respectively; these values were higher than those of the solvent-cast films. The tensile strength values varied from ca. 5 to 53 MPa with decreasing acyl carbon number, and the elongation at break values tended to increase with increasing acyl carbon number. These dependences on acyl carbon number were similar to those of the solvent-cast films. Serious thermal degradation did not occur during heating. These data mean that the mechanical properties of GM esters could be controlled by the structure of the acyl group. These GM esters could be used as novel bio-based plastic materials.

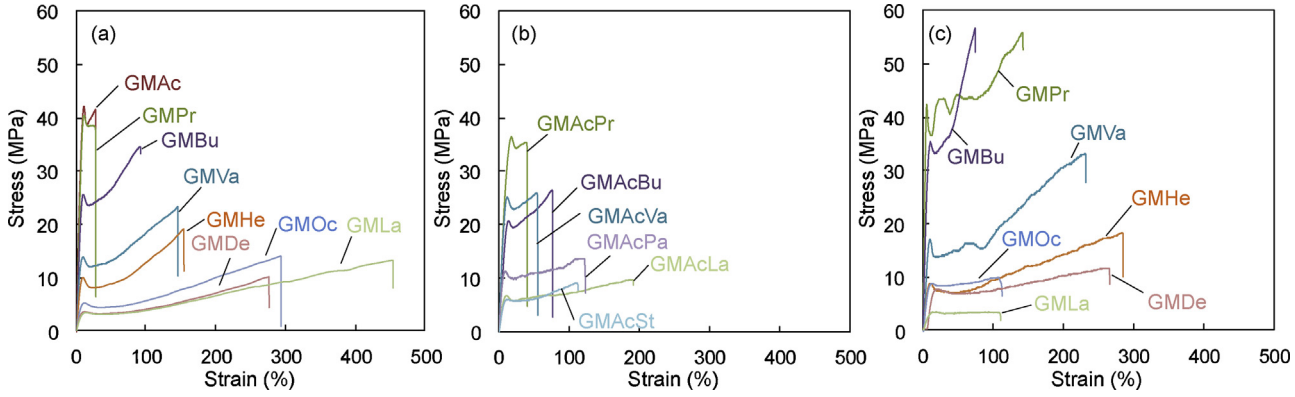

Fig. 6. Stress–strain curves of solvent-cast films of (a) GM homoesters and (b) GM mixed esters, and (c) thermo-pressed films of GM homoesters.

4. Conclusions

GM homoesters (GMAc to GMLa) were prepared from KGM treated in a carboxylic acid/TFAA mixed system. GM acetyl/acyl mixed esters (GMAcPr to GMAcSt) were prepared from KGM treated in a mixed acetic acid/carboxylic acid/TFAA system. The DS values were calculated from ^{1}H NMR analysis. TGA revealed that the thermal stability of KGM was improved by acylation. DSC and X-ray diffraction measurements showed that the GM esters were amorphous. The T_gs of the GM esters decreased with increasing acyl carbon number. DMA measurements suggested that relaxation of alkyl side-chains occurred below T_gs. Colorless and transparent films of the GM esters were obtained by both solvent casting and thermo-pressing. The tensile strengths and Young's moduli of the films decreased with increasing acyl carbon number. The elongation at break of the esters increased with increasing acyl carbon number. These results implied that the thermal and mechanical properties of the GM esters can be controlled by the structure of the acyl group. These GM esters could have practical applications as bio-based plastic materials.

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