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Syntheses and characterization of konjac glucomannan acetate and their thermal and mechanical properties

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ABSTRACT

Fully substituted glucomannan triacetate (GMTAc) (degree of substitution (DS) = 3.0) was prepared from konjac glucomannan (KGM) treated with acetic acid and trifluoroacetic anhydride (TFAA). The peaks in the ^{1}H- and ^{13}C NMR spectra of GMTAc were assigned in detail based on two-dimensional (DQF-COSY, HSQC and HMBC) NMR analysis. Glucomannan acetate samples (GMAc) with different degrees of substitution (DS = 1.3, 1.7, 2.0 and 2.8) were prepared by partial deprotection of GMTAc. Thermal properties of GMAcs including GMTAc were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Their decomposition temperatures were higher than that of KGM, and increased with increase in DS. DSC measurements revealed that GMAc had a high glass transition temperature in the range of 178–219 °C, which decreased with increase in DS. The samples did not exhibit melting peaks, indicating that the GMAcs were amorphous. All GMAcs formed transparent films upon solvent casting, and tensile tests revealed that GMAc had a higher tensile strength and elongation to break at lower DS (1.3 and 1.7) compared to higher DS (2.0, 2.8 and 3.0). This means that the mechanical properties of GMAc could be controlled by DS.

1. Introduction

Konjac glucomannan (KGM) is a natural polysaccharide isolated from 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 and Matsuda, 1969; Maeda et al., 1980; Smith and Srivastava, 1959). Katsuraya et al. have proposed that one branching position is the C6 position of the glucosyl unit (Katsuraya, Okuyama, Hatanaka, Oshima, Sato, & Matsuzaki, 2003).

KGM has a high molecular weight (more than 1,000,000 Da), is water soluble, forms gels readily, and is biodegradable and biocompatible. Owing to 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, chitin or KGM, 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, esterification is known to be an effective way to obtain thermoplastic material, and cellulose esters, such as acetate, are widely used in industry (Morooka, Norimoto, Yamada, & Shiraishi, 1984; Sealey, Samaranayake, Todd, & Glasser, 1996). In most studies, unmodified KGM has been used in films, membranes or gels or blended with other polymers (Fan, Zheng, Xu, Huang, & Zhang, 2007; Xiao, Lu, & Zhang, 2001). There have been a few studies on esterification reactions of KGM, such as acylation. For example, preparation of GM acetates with low degrees of substitution and their gelation or water absorbency properties were reported (Chen, Zong, & Li, 2006; Du, Li, Chen, & Li, 2012; Hannuksela, & du Penhoat, 2004; Koroskenyi, & McCarthy, 2001; Liu et al., 2012). Highly substituted KGM esters are promising candidate bio-based thermoplastic materials in industry as well as cellulose esters.

In the present study, we present the syntheses of fully and partially acetylated glucomannan derivatives, with the aim to prepare thermoplastic materials from KGM. Efficient acetylation of freeze-dried KGM was carried out in an acetic acid and trifluoroacetic anhydride (TFAA) mixed system. Glucomannan acetates with different degrees of substitution were prepared by deprotection of the fully acetylated glucomannan. Films were made from the obtained glucomannan acetates, and their thermal and mechanical properties were determined.

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2. Experimental

2.1. Materials

Konjac glucomannan (KGM) (Propol® A) was kindly provided by Shimizu Chemical, Co. (Hiroshima, Japan). Trifluoroacetic anhydride (TFAA), acetic acid, 1,8-diazabicyclo[5,4,0]-7-undecene (DBU) and all other reagents were commercially obtained and used without further purification.

2.2. Preparation of glucomannan triacetate (GMTAc) (DS = 3.0)

KGM (0.5 g) was dissolved in water (100 ml) at 65 °C and freeze-dried. A pre-mixed solution of trifluoroacetic anhydride (TFAA), (20 ml) and acetic acid (20 ml), which had been stirred at 50 °C for 20 min, was immediately added to the freeze-dried KGM 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 re-precipitated in ethanol, before finally being filtered, washed with ethanol and dried in vacuo to give glucomannan triacetate (GMTAc, where Ac represents the acetyl group) (0.76 g, 85% yield, $M_n = 3.0 \times 10^5$, $M_w = 5.6 \times 10^5$, $M_w/M_n = 1.9$). The number average degree of polymerization (DP_n) was calculated as 1.0×10^3 by dividing the number average molecular weight of GMTAc by the molecular weight of an acetylated anhydroglucose and mannose unit (288.3). The degree of substitution (DS) of the acetyl groups was calculated to be 3.0 from the ratio of the integrated areas of the methyl protons of the acetyl group to the ring protons of glucose and mannose, as follows: DS = ([CH_3]/3)/([ring-H]/7). ^{1}H-NMR ($CDCl_3$): δ 1.94, 2.02, 2.11 (CH_3), 3.55 (C5—H (G, M—M, G—M)), 3.79 (C4—H (G—G, M—G, G—M)), 3.89 (C4—H (M—M)), 4.07, 4.19, 4.30, 4.38 (C6—H (G, M)), 4.44 (C1—H (G—G)), 4.51 (C1—H (G—M)), 4.59 (C1—H (M—G)), 4.68 (C1—H (M—M)), 4.81 (C2—H (G)), 5.04 (C3—H (M—M, G—M)), 5.10 (C3—H (M—G, G—G)), 5.34 (C2—H (M—M, G—M, M—M, M—G)). ^{13}C-NMR ($CDCl_3$): δ 20.4, 20.5, 20.6 (CH_3), 62.2, 62.6 (C6 (G, M)), 68.3, 68.5, 68.6 (C2 (M—M, G—M, M—M, M—G)), 70.6, 70.8 (C3 (M—M, G—M)), 71.6, 71.8 (C2 (G)), 72.0, 72.1 (C3 (G)), 72.8 (C4 (M—M)), 72.8, 73.1 (C5 (G, M—M, G-M)), 73.8 (C4 (G—M)), 74.4 (C4 (M—G)), 75.9 (C4 (G—G)), 97.3, 97.4, 97.6, 97.9 (C1 (M—M, M—G)), 100.3, 100.5 (C1 (G—G, G—M)), 169.2–170.5 (C=O).

2.3. Preparation of glucomannan acetate samples with different DS

GMAcs with different DS were prepared by partial deacetylation of GMTAc with DS of 3.0. A representative procedure for obtaining GMAc (DS = 2.8) is as follows: 1,8-diazabicyclo[5,4,0]-7-undecene (DBU) (0.37 ml) was added to a solution of GMAc (0.864 g) in *N*,*N*-dimethylformamide (DMF) (64 ml) and methanol (16 ml) at 40 °C, and stirred for 2 h. The solution was poured into ethanol (1.0 l). The precipitate was filtered, washed with ethanol, and dried in vacuo to give GMAc (DS = 2.8). GMAcs (DS = 1.3 and 2.0) were obtained using DBU (1.1 and 0.74 ml), respectively. Further detailed control of DS by varying the DBU amount was difficult in this system because of gelation. GMAc with DS of 1.7 was obtained using DBU (3.0 ml) in *N*,*N*-dimethylacetamide (DMAc) (64 ml).

2.4. Determination of DS of glucomannan acetate

Some of the partially deacetylated GMAcs were insoluble in chloroform. To enable the determination of DS by NMR analysis, the free hydroxyl groups of partially deacetylated GMAcs were completely propionylated to improve their solubility. A representative procedure is as follows: partially deacetylated GMAc (10 mg) was added to a solution of propionic anhydride (0.5 ml) in pyridine (0.5 ml), at 50 °C, and stirred for 5 h. The solution was poured into ethanol (15 ml). The precipitate was filtered, washed with ethanol, and dried in vacuo to give per-propionylated GMAc. The degree of substitution of acetyl groups was calculated from the ratio of the integrated areas of the methyl protons of the acetyl group to the ring protons of glucose and mannose, as follows: DS = ([CH_3(Ac)]/3)/([ring-H]/7).

2.5. Nuclear magnetic resonance (NMR) measurements

^{1}H, ^{13}C, DQF-COSY (double quantum filtered correlation spectroscopy), HSQC (heteronuclear single quantum coherence) and HMBC (heteronuclear multiple bond correlation) NMR spectra were recorded with a JEOL JNM-A500 FT-NMR (500 MHz) spectrometer at 25 °C, using chloroform-*d* as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and coupling constants (*J*) are reported in (ppm) and (Hz), respectively.

2.6. Gel permeation chromatography (GPC) measurement

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

2.7. Thermogravimetric (TGA) analysis

Thermogravimetric 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.

2.8. Differential scanning calorimetry (DSC) measurement

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

2.9. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) measurements were performed with a DVA-200S analyzer (IT measurement control, Japan). Temperature scans at 1 Hz frequency were carried out with the range of −150 °C to 300 °C at heating rate 5 °C/min under a nitrogen atmosphere. Specimens (18 × 5 mm) were prepared from cast films.

2.10. Solubility test

Samples (10 mg) were dissolved in a solvent (1 ml) at room temperature. *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chloroform, acetone, ethanol and water were used for the tests.

2.11. Tensile test

Tensile tests of GMAc cast-films were carried out at room temperature using an EZ-test (Shimadzu, Japan). The crosshead speed

was 20 mm/min, and the initial gauge length was 10 mm. Five specimens (25 × 4 mm) were used for each measurement, and the data were averaged for each composition.

2.12. Preparation of solvent-cast films

GMAcs (0.4 g) were dissolved in DMF (15 ml), and poured into teflon plates (4 cm diameter). The solvent was then evaporated in vacuo at 50 °C.

3. Results and discussion

3.1. Preparation of glucomannan triacetate (DS = 3.0)

KGM is soluble in water, but insoluble in organic solvents such as DMF or DMSO. KGM showed low solubility in a DMAc/lithium chloride system, which is known to be a good solvent for homogeneous esterification of cellulose (McCormick & Callais, 1987). A mixture of carboxylic acids and TFAA is another efficient esterification system for cellulose (Morooka et al., 1984; Tsuzuki, Shiraishi, & Yokota, 1980), but the as-received KGM did not dissolve in acetic acid and TFAA solution, probably because the KGM had adsorbed water and strong hydrogen bonding. Therefore, KGM was pretreated by dissolving in water and freeze-drying. The acetic acid and TFAA mixed solution was immediately added to the freeze-dried KGM in a flask, to minimize problems from water adsorption. The freeze-dried KGM dissolved easily in the solution at 50 °C, and a homogeneous solution was obtained within 30–60 min. Pretreatment such as freeze-drying appears necessary to allow easy access of the reagents to the GM molecules and enable efficient esterification; a similar effect was previously reported for starch (Yang & Montgomery, 2006). In the FT-IR spectrum of the obtained compound, the absence of OH absorption at $\nu = 3446\ cm^{-1}$ and the presence of C=O absorption at ca. $1750\ cm^{-1}$ were indicative of successful esterification of KGM (data not shown). ^{1}H and ^{13}C NMR spectra of the obtained compound were measured, and the peaks assigned according to DQF-COSY, HSQC and HMBC NMR analysis, as shown in Figs. 1 and 2. Detailed assignment is discussed in the following section. The NMR measurements revealed that fully substituted glucomannan triacetate (GMTAc) was successfully obtained. The degree of substitution (DS) of the acetyl groups was calculated as 3.0 using the integrated areas as discussed above. The M_n, M_w and M_w/M_n of GMTAc were 3.0×10^5, 5.6×10^5 and 1.9, respectively. DP_n of GMTAc was calculated as 1.0×10^3 by dividing M_n by the molecular weight of the acetylated anhydroglucose and mannose unit (288.3).

3.2. Detailed NMR analysis of glucomannan triacetate

The peaks in the ^{1}H and ^{13}C NMR spectra of GMTAc were carefully assigned, based on the DQF-COSY, HSQC and HMBC spectra, as shown in Figs. 1 and 2. In the ^{13}C-NMR spectrum, no peaks corresponding to original un-substituted KGM (Katsuraya et al., 2003) were observed, and the chemical shifts were different from those of partially acetylated KGM (Chen et al., 2006).

The previous study on ^{13}C-NMR analysis of KGM revealed that the C1 carbon of mannose unit is observed upfield from that of the glucose unit (Katsuraya et al., 2003). Therefore, two major peaks at 98 and 102 ppm were assigned to C1 carbons of mannose (M) and glucose (G) units, respectively, as shown in Fig. 2. It has been reported that the proton and carbon signals of glucose and mannose units are observed at different chemical shifts because of the differences in the structure (G, M) and the sequence of sugar units (G—G, G—M, M—G and M—M) (Katsuraya et al., 2003). Based on the correlation in the HSQC spectrum, C1—H(M) and C1—H(G) were assigned as shown in Fig. 2a. C1(M) was correlated with two proton peaks, and these protons were assigned as C1—H(M—M) (4.68 ppm) and C1—H(M—G) (4.59 ppm). According to the correlation of C1 carbons in the HMBC spectrum (Fig. 2b), the proton peaks C2—H(G) (4.81 ppm) and C2—H(M) (5.34 ppm) were assigned. Glucose and mannose have a hydroxyl group at the C2 position, with equatorial and axial configurations, respectively. C2—H(M) was observed as the furthest downfield of the ring-protons. In the DQF-COSY spectrum (Fig. 1b), C2—H(M) showed two major correlations with C3—H(M) (5.04 ppm), whilst the C3—H(M) proton was correlated with both C4—H(G—M) (3.79 ppm) and C4—H(M—M) (3.89 ppm). Similarly, C2—H(G) correlated with both C1—H(G—G) (4.41 ppm) and C1—H(G—M) (4.51 ppm). These correlations support the existence of different sequences of sugar units.

The NMR analysis enabled detailed assignment of the protons and carbons at the C1 and C4 positions, depending on the sequence. In the HMBC spectrum, correlations between C1 of one unit and C4—H of a neighboring unit were clearly observed. The split peaks of C1(M—M, M—G) (98 ppm) correlated with C4—H(M—G) (3.79 ppm) and C4—H(M—M) (3.89 ppm), as indicated by the red dashed lines in Fig. 2b. The correlations between C1(G—G, G—M) (102 ppm) and C4—H (G—G, G—M) were observed as one peak. Three correlations between C4(G—M), C4(M—G) and C4(M—M) carbons and the corresponding C4-H protons were also observed in the HSQC spectrum (Fig. 2a). Subsequently, four C4 carbon peaks, namely C4(G—G), C4(G—M), C4(M—G) and C4(M—M), were assigned. Correlations between C1—H of one unit and C4 of a neighboring unit were observed as before. The four peaks of the C4 carbons correlated with the corresponding neighboring C1—H protons in the HMBC spectrum, as indicated by dashed lines in Fig. 2b. The correlations between C4 carbons and C2—H, C3—H and C5—H protons in the HMBC spectrum support these assignments. The carbon peaks at 72.4 ppm and 72.6 ppm could not be assigned from the two dimensional NMR spectra, because of the absence of any clear correlations. The split C5 carbons may be overlapping the C4(M—M) carbon at 72.8 ppm, but it was difficult to assign all C5 carbons completely. Branching positions could not be determined from our NMR data.

Proton peaks at 1.9 ppm, 2.0 ppm and 2.1 ppm were assigned as methyl protons (CH_3) of the acetyl group. Three main carbon peaks at 20.4 ppm, 20.5 ppm and 20.6 ppm correlated these three protons in both the HSQC and HMBC spectra. Three major correlations between CH_3 protons and carbonyl carbons (C=O) (169.2–170.0 ppm) were also observed. In the case of cellulose triacetate, three main peaks from carbonyl carbons are assigned in order of C6, C3 and C2, with C6 the furthest downfield (Heinze & Liebert, 2004). However, in the case of GMTAc, it seems that the C=O carbons in the HMBC spectrum did not appear in the same order as was found for cellulose acetate. The C=O signal from C2(M) appeared further downfield than that of C3(M), and was overlapping the signal from C3(G). In addition, a shoulder was observed for on the CH_3 proton peak (2.1 ppm), the CH_3 and C=O carbon peaks were split, and the areas of the three CH_3 proton peaks are not equal. These facts suggest that the acetyl protons, acetyl carbons and carbonyl carbons appeared at different chemical shifts or overlapped, depending on the structure of the sugar unit, its neighboring unit, and the substituted positions. It was difficult to completely assign the acetyl and carbonyl protons and carbons.

3.3. Glucomannan acetate with different DS values

As described above, GMAcs with different DS values were prepared. The samples were propionylated and then ^{1}H-NMR spectra were measured in chloroform. A representative spectrum is shown in Fig. 3. Degrees of substitution were calculated from peak areas as

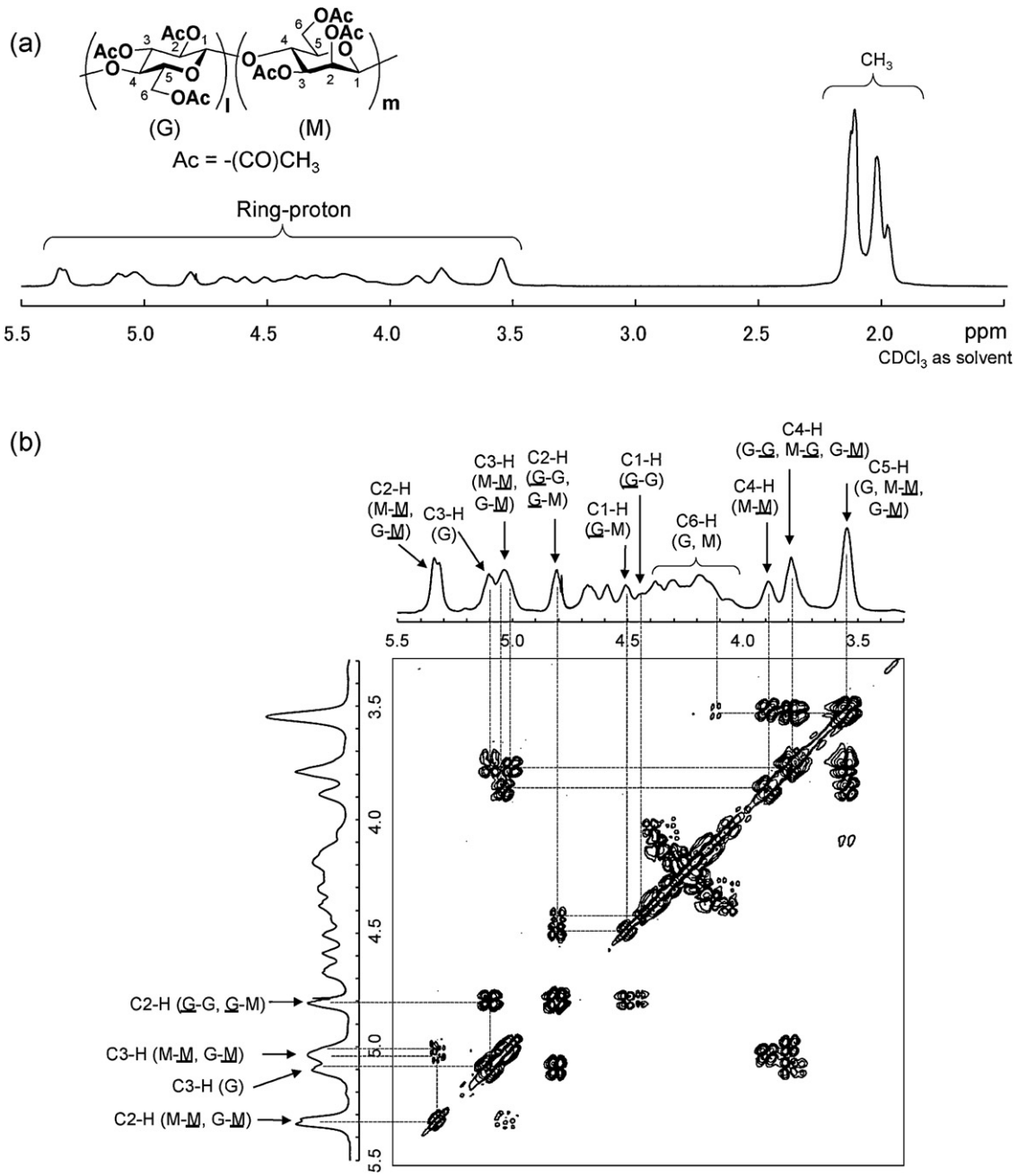

Fig. 1. (a) ^{1}H-NMR spectrum and (b) DQF-COSY spectrum of the ring-proton region of GMTAc. G: glucose, M: mannose, G—G, G—M, M—G, M—M: β(1 → 4) linked glucose and/or mannose units.

described previously. GMAc samples with four different DS values (1.3, 1.7, 2.0 and 2.8) were obtained.

3.4. Thermal properties

The thermal behavior of the GMAcs was analyzed by DSC and TGA measurements. The TGA thermograms are shown in Fig. 4a. The decomposition temperature at 50% weight loss for the GMAc with DS value of 1.3 was 330 °C, similar to that of GM (329 °C). The decomposition temperatures for the DS 2.8 sample (372 °C) and the GMTAc (DS = 3.0) sample (375 °C) were also very close together The decomposition temperatures at 50% weight loss for GMAcs with DS values of 1.7 and 2.0 were 350 °C and 351 °C, respectively, intermediate between the temperatures for GMTAc (DS = 3.0) and GM. The decomposition temperatures of GMAcs did not show linear increase with increasing DS, probably because they were also affected by hydrogen bonding between hydroxyl groups, but tended to increase with increasing DS value; the thermal stability of GM was improved by acetylation.

Fig. 4b shows the second heating cycles of the DSC thermograms of the GMAcs. The heating rate was set to 100 °C/min, because no glass transition (T_g) was observed at the usual heating rates of 10 or 20 °C/min. This fact suggests that the molecular motion of the chains associated with the glass transition of the GMAc samples is quite restricted. In representative dynamic mechanical analysis (DMA) of GMTAc at a scan rate of 5 °C/min, the storage modulus (E') showed a marked drop, accompanied with a loss tangent (tan δ) peak at the temperature that corresponds to glass transition (T_g) measured by DSC (Fig. 4c). The T_gs measured by DSC at 100 °C/min should not be particularly different from those

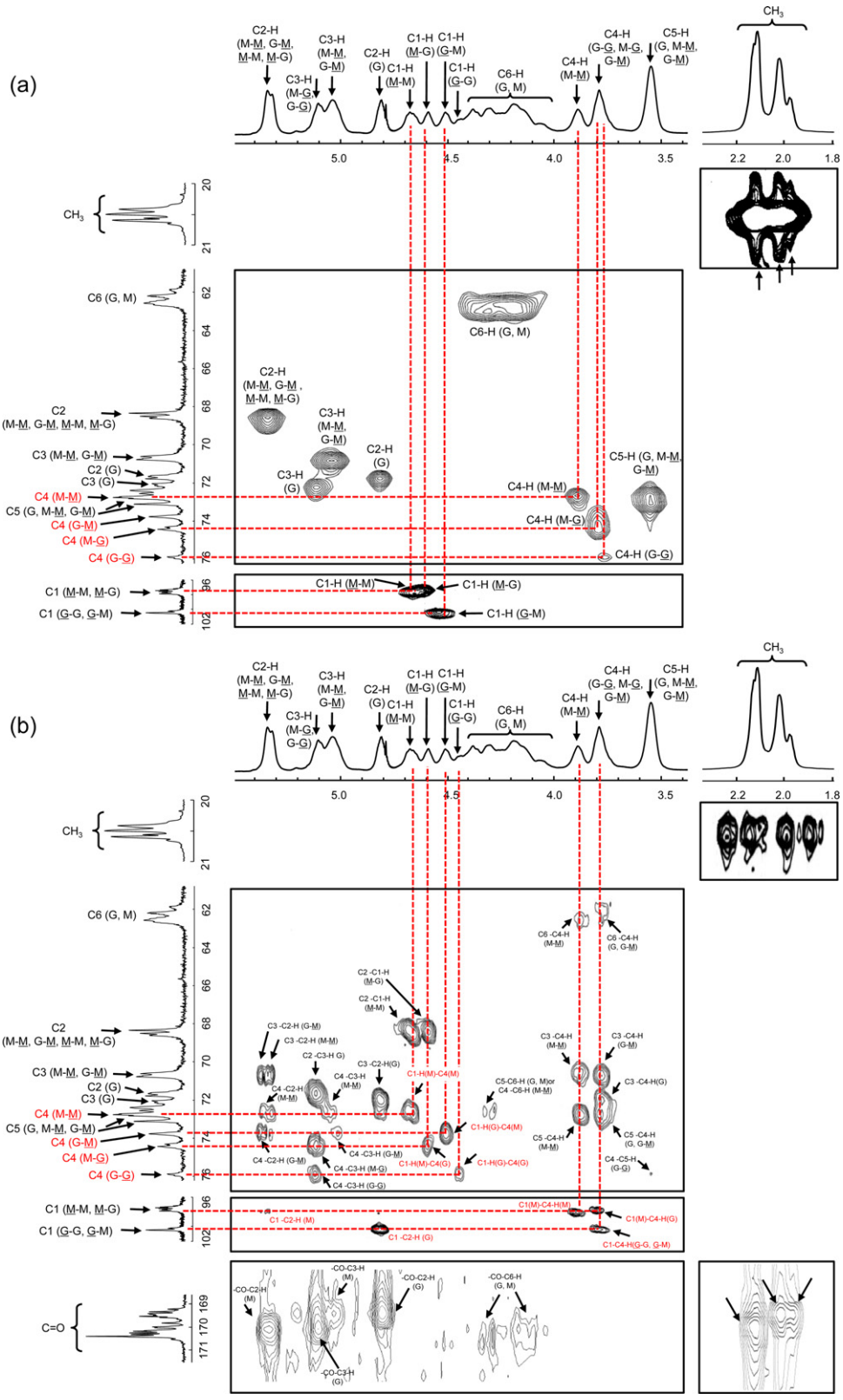

Fig. 2. (a) HSQC and (b) HMBC NMR spectra of GMTAc. G: glucose, M: mannose, G—G, G—M, M—G, M—M: β(1 → 4) linked glucose and/or mannose units.

measured at lower scan rates. The GMAcs showed no melting point, indicating that they were amorphous. X-ray diffraction analysis supported the conclusion that the GMAcs were amorphous (data not shown). In addition, the GMAcs exhibited quite high T_g values, ranging from 178–219 °C, depending on the DS value. The T_g values decreased with increasing DS. This is because samples with lower DS probably have stronger hydrogen bonding between their hydroxyl groups. These T_gs were higher than those reported for other amorphous polymers, such as polystyrene (PS) (ca. 100 °C) or poly(methyl methacrylate) (PMMA) (ca. 106 °C) and comparable

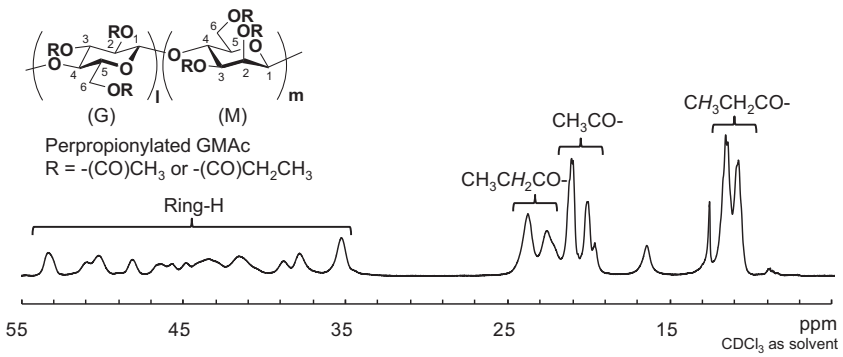

Fig. 3. ^{1}H-NMR spectrum of perpropionylated GMAc (DS = 1.3). G: glucose, M: mannose.

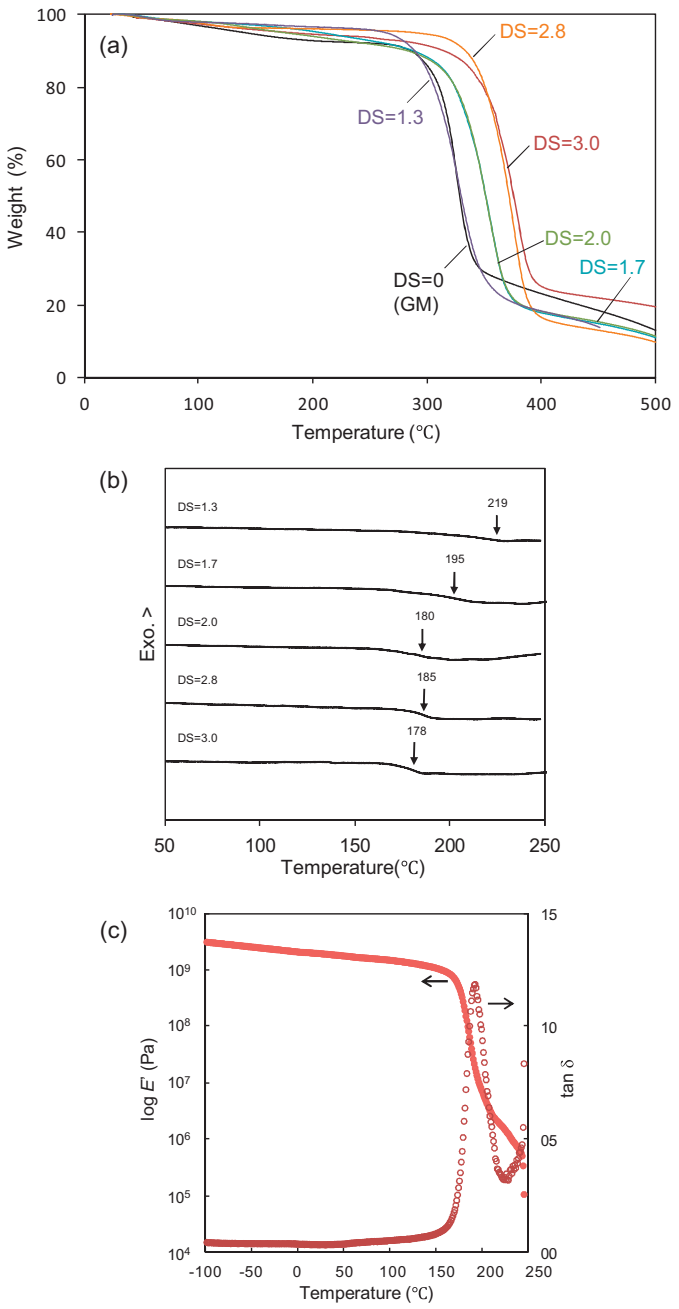

Fig. 4. (a) TGA, (b) DSC thermograms of GMAcs and GM, and (c) representative plots of storage modulus (E') (●) and loss tangent (tan δ) (○) of GMTAc.

with that of cellulose triacetate (ca. 180 °C) (Billmeyer, 1984; Mark, 1996). These data demonstrated that GMAcs are novel amorphous polymers having high T_g.

3.5. Solubility

Solubility of GMAcs was investigated and the results are listed in Table 1. KGM was soluble in water and insoluble in common organic solvents. All GMAcs were insoluble in water, even at low DS, and soluble in polar organic solvents, such as DMF, DMAc and DMSO. The GMAc samples with DS values of 3.0 and 2.8 had higher solubility in other organic solvents, such as chloroform, acetone, and THF. Acetylation made KGM more hydrophobic, and improved its solubility in organic solvents; the final solubility depended on the DS value.

3.6. Mechanical properties of GMAc films

Films of GMAcs were obtained by solvent-casting from DMF solutions under reduced pressure. Fig. 5 shows a representative image of the films of GMAc samples with DS values of 1.3 and 3.0. The GMTAc film was transparent and colorless. Films of GMAc with lower DS were transparent and slightly brown in color. The strain-stress curves of the GMAc films are shown in Fig. 6, and their tensile properties are listed in Table 2. Interestingly, GMAcs with lower DS values (1.3 and 1.7) exhibited higher tensile strength

Table 1
Solubility of GMAcs.

Solvent	DS of GMAcs				
	1.3	1.7	2.0	2.8	3.0
DMAc	+	+	+	+	+
DMF	+	+	+	+	+
DMSO	+	+	+	+	+
THF	–	–	–	+	+
Chloroform	–	–	–	+	+
Acetone	–	–	–	+	+
Ethanol	–	–	–	–	–
Water	–	–	–	–	–

+: soluble, –: insoluble.

Table 2
Mechanical properties of GMAc films.

DS of GMAcs	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
1.3	76 ± 4	31 ± 4	0.98 ± 0.09
1.7	67 ± 12	22 ± 7	0.95 ± 0.21
2.0	48 ± 9	19 ± 9	0.84 ± 0.09
2.8	46 ± 2	12 ± 3	0.81 ± 0.17
3.0	52 ± 3	13 ± 3	0.87 ± 0.04

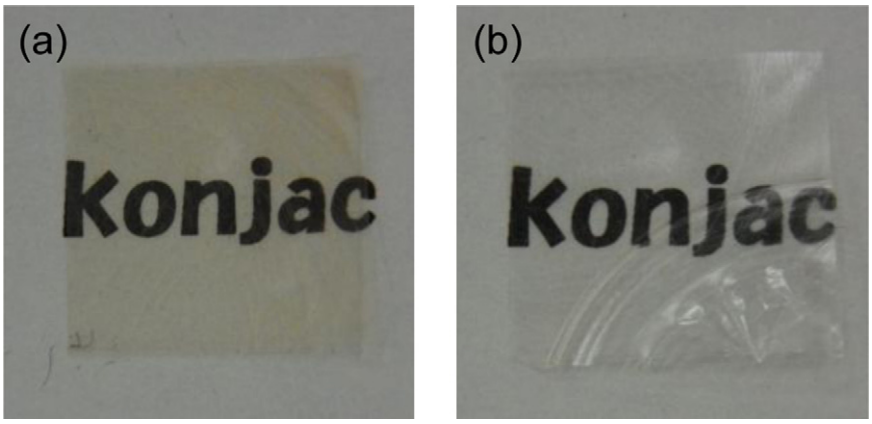

Fig. 5. Images of the cast films of (a) GMAc (DS = 1.3) and (b) GMTAc (DS = 3.0).

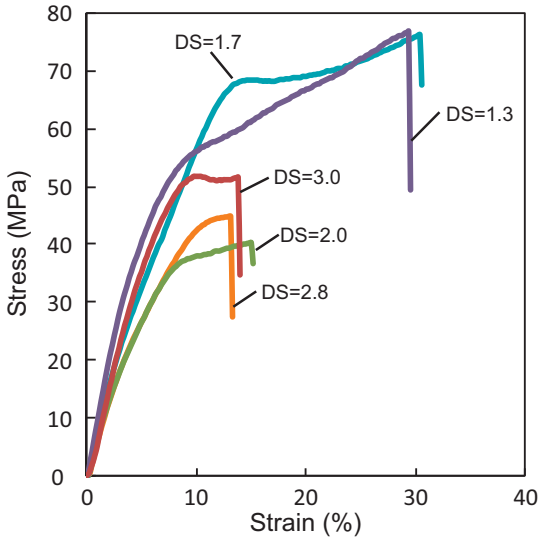

Fig. 6. Stress-strain curves of GMAc films.

and elongation at break, compared to GMAcs with higher DS (2.0, 2.8 and 3.0). Tensile properties seem to be strongly affected by hydrogen bonding between hydroxyl groups. This suggested that the mechanical properties of GMAc could be controlled by DS. The tensile strength of GMAc samples with higher DS (2.0, 2.8 and 3.0) (46, 48 MPa and 52 MPa) and lower DS (1.3 and 1.7) (67 MPa and 76 MPa) were comparable with those of PS (30–60 MPa) and PMMA (50–70 MPa), respectively (Billmeyer, 1984; Mark, 1996). In addition, values of elongation at break of GMAc films (12–31%) were higher than those of PS (1–4%) or PMMA (2–10%). GMAcs are a new class of plastics that show high mechanical properties; they are also expected to be biodegradable, like cellulose acetate (Buchanan, Gardner, & Komarek, 1993).

4. Conclusion

Glucomannan triacetate (GMTAc) with DS of 3.0 was prepared from konjac glucomannan (KGM) treated with acetic acid and TFAA. The peaks in the ^{1}H and ^{13}C NMR spectra of GMTAc were assigned in detail based on two-dimensional NMR analysis. GMAcs with different DS (1.3, 1.7, 2.0 and 2.8) were prepared by partial deprotection of GMTAc. The thermal stability of the GMAcs increased with increasing DS. DSC measurements revealed that GMAcs were amorphous and had high glass transition temperatures, above those of other amorphous polymers such as PS or PMMA. Tensile tests of GMAc films revealed that GMAc samples with lower DS (1.3 and 1.7) had higher tensile strength and elongation at break values compared to those of higher DS samples (2.0, 2.8 and 3.0). This implies that the mechanical properties of GMAc can be tailored by varying the DS.

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