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Thermal and mechanical properties of tailor-made unbranched α-1,3-glucan esters with various carboxylic acid chain length

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ABSTRACT

The convenient and environmentally friendly method for *in vitro* polymerization catalyzed by glucosyltransferase, designated as GtfJ, extracted from recombinant *E. Coli* was used to synthesize tailor-made α-1,3-glucan (α-1,3-D-glucan) having moderate molecular weight ($M_w = 2.0 \times 10^5$) and no branches. With the aim to improve thermoplasticity of this polysaccharide, after *in vitro* synthesis, chemical modification by acylation was selected and then fully substituted α-1,3-glucan esters were successfully obtained via both homogeneous and heterogeneous methods. Thermal degradation temperature of α-1,3-glucan esters was improved after esterification and dependent on neither side chain length nor synthesis methods. DSC curves suggested a presence of crystal structure in α-1,3-glucan acetate, propionate, butyrate, valerate and hexanoate due to detectable melting endotherm, whereas octanoate exhibited amorphous behavior. T_m's of α-1,3-glucan esters were relatively high, more than 200 °C, in comparison with commercial plastics. The shorter chain length of acid component, the higher T_m and T_g ester products exhibited. In addition, tensile strength of α-1,3-glucan esters decreased in contrast with elongation at break with an increase in alkyl chain length of an acid component. Thus, crystalline and amorphous α-1,3-glucan esters with adjustable thermal and mechanical properties obtained from this research are promising materials for continuing applied researches and contemplating the future application in bio-based thermoplastic materials.

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1. Introduction

Oil depletion, oil price fluctuations and environmental concerns caused by the consumption of traditional petroleum-based polymers have been raised as global issues so far (Caldara, Cavallo, & Iacoviello, 2016; Thompson, Moore, Vom Saal, & Swan, 2009). Recently, The Intergovernmental Panel on Climate Change (IPCC) suggested mitigating the green house gas emission to limit the temperature rise not more than 2 °C before year 2050 (Edenhofer et al., 2014). With these ecological and economic concerns, many researchers have been attempting to explore new sorts of materials especially bio-based polymers to substitute those from oil derivatives (Berezina & Martelli, 2014).

Having been researched extensively, bio-based polymers are regarded as the materials for sustainability and environmental benignity (Berezina & Martelli, 2014; Iwata, 2015; Sudesh & Iwata, 2008). Generally, bio-based polymers can be produced from various bioresources such as plants, animals and microorganisms. The production of bio-based polymers can currently be classified into two distinct routes (Berezina & Martelli, 2014). The first route is the production of bio-based monomers followed by the polymerization such as the synthesis of polylactic acid (PLA) from bio-based lactic acid (Dusselier, Wouwe, Dewaele, Makshina, & Sels, 2013) and of polybutylene succinate (PBS) from bio-based succinic acid (Cok, Tsiropoulos, Roes, & Patel, 2014; Lee, Kim, Choi, Yi, & Lee, 2011). Both of them have been already commercialized at present. Furthermore, some commonly used polymers in our daily lives can also be produced from bio-based resources such as the production of well-known polyethylene (PE) from bio-based ethanol by Brazilian company Braskem (Morschbacker, 2009) and the production of polyamides (PA) from bio-based caprolactam (Berezina & Martelli, 2014; Turk et al., 2016). Another route for producing bio-based polymers is a direct synthesis by living organisms, which

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produce mostly polysaccharides, such as cellulose from plants, chitosan from fungi and crustacean, and polyhydroxyalkanoates (PHA) and extracellular polysaccharides (EPS) from microorganisms.

With benefit from natural abundance, polysaccharides have gained much interest because they are the basic component of natural living organisms, non-toxic and also biodegradable, and EPS or exopolysaccharides have been becoming more attractive as a force driven by green initiatives to find new structural polysaccharides other than well-known cellulose for various material applications. Generally, microorganisms produce EPS for biofilm formation, cell-to-cell interaction and cell protection (Kumar, Mody, & Jha, 2007). The utilization of EPS has been found in some applications such as xanthan (β-1,4-D-glucan with β-D-mannose-1,4-β-D-glucuronic acid-1,2-α-D-mannose side chain) from *Xanthomonas* in secondary and tertiary crude-oil recovery and in food as thickening and stabilizing agent (Palaniraj & Jayaraman, 2011), dextran (α-1,6-D-glucan; some 1,2-, 1,3-, or 1,4-linkages) from *Leuconostoc mesenteriodes* as blood plasma extender and molecular sieve (Sarwat, Qader, Aman, & Ahmed, 2008), gellan (α-1,3-linkages of tetrasaccharide units; partially O-acetylated D-glucose-1,4-β-glucuronic acid-1,4-β-D-glucose-1,4-β-L-rhamnose) from *Sphingomonas paucimobilis* for solidifying culture media (Bajaj, Survase, Saudagar, & Singhal, 2007), and curdlan (β-1,3-D-glucan) from *Alcaligenes faecalis* and *Agrobacterium* as a gelling agent and an immobilization matrix (Lee, 2005). However, the limitation of the direct production of EPS by microorganisms is the difficulty in structure and composition control due to the nature of each producer. For this reason, most of EPS have branching structures (Aires et al., 2011; Sutherland, 2002), which affect mechanical and thermal properties of materials and limit their possible applications.

To find new unnatural-type polysaccharides, genetic engineering has been introduced and applied for producing distinctive enzymes for synthesis of tailor-made EPS with the prospect to be utilized as high-performance renewable green materials for various applications (Schmid, Sieber, & Rehm, 2015). Recently, the production of man-made α-1,3-glucan (α-1,3-D-glucan) by *in vitro* polymerization with glucosyltransferase J enzyme, GtfJ, from *Streptococcus salivarius* ATCC 25975 has been reported (Puanglek et al., 2016). With the GtfJ enzyme, this production needs only a renewable carbon resource such sucrose and the reaction is conducted in water system under designated pH and temperature. The structure of *in vitro* synthesized α-1,3-glucan is completely linear without branching structure. However, this material is insoluble in most organic solvents and thermal unprocessable, therefore it was chemically modified to α-1,3-glucan acetate and propionate. The results showed that these two ester derivatives had superior melting and glass transition temperature over commercial plastics. Consequently, for further studies, the effect of various acid chain length of this material, the synthesis methods, structure-related mechanical and thermal properties are major priorities for investigation in order to adjust this material for desired properties of plastics in either forms of films or fibers.

In this research, unbranched α-1,3-glucan was *in vitro* synthesized using GtfJ enzyme from *Streptococcus salivarius* ATCC 25975 for preparation of starting material. Then, the series of ester derivatives having different acid chain length were synthesized via homogeneous and heterogeneous methods. Furthermore, the thermal and mechanical properties of α-1,3-glucan ester films were investigated. Hopefully, this material could be a substitution product to come on board replacing petroleum-derived plastics so as to avoid the uncertainty and sensitivity from oil's booms and busts, mitigate the environmental issues and create the sustainability for future generations.

2. Experimental

2.1. Materials

Sucrose, imidazole, ampicillin sodium, isopropyl β-D-1-thiogalactopyranoside (IPTG), sodium chloride (NaCl), ammonium sulfate ($(NH_4)_2SO_4$), lysozyme, dithiothreitol (DTT), *N,N*-dimethylacetamide (DMAc), trifluoroacetic anhydride (TFAA) and lithium chloride (LiCl) were purchased from Wako Pure Chemical Industries, Ltd. Protease inhibitor (cOmplete™, EDTA-free) was acquired from Roche Diagnostics. Carboxylic acids and acid anhydrides (acetic, propionic, butyric, valeric, hexanoic and octanoic) were provided by commercial supplier and used without further purification.

2.2. In vitro *synthesis of α-1,3-glucan*

Escherichia coli (*E. coli*) BL21-Gold (DE3) (Stratagene, USA) with pET-21a(+) (Novagen, USA) vector, expressing GtfJ cloned from *Streptococcus salivarius* ATCC 25975, were cultured to produce GtfJ enzyme for the *in vitro* synthesis of α-1,3-glucan. The procedures for bacteria culture, purification of enzyme and *in vitro* synthesis of α-1,3-glucan are stipulated in the previous paper (Puanglek et al., 2016). ^{1}H and ^{13}C NMR peaks of *in vitro* synthesized α-1,3-glucan are reported as follows.

α-1,3-Glucan. ^{1}H NMR (500 MHz, DMSO-*d*6, *δ*, ppm): 3.41 (H-2, H-4), 3.51 (H-6a), 3.62 (H-3, H-6b), 3.82 (H-5), 4.25 (OH-C6), 4.52 (OH-C2), 4.92 (OH-C4), 5.06 (H-1).

α-1,3-Glucan. ^{13}C NMR (500 MHz, DMSO-*d*6, *δ*, ppm): 60.2 (C-6), 69.5 (C-4), 70.9 (C-2), 72.0 (C-5), 82.9 (C-3), 99.9 (C-1).

2.3. Synthesis of α-1,3-glucan esters

2.3.1. Esterification of α-1,3-glucan by a heterogeneous method

TFAA (20 mL) and carboxylic acid (20 mL) were pre-mixed and stirred at 50 °C for 10 min. Dried α-1,3-glucan (0.5 g) was added to the pre-mixed solution and the mixture was then continually stirred at 50 °C for 3 h. After the reaction, the solution was cooled to room temperature and then slowly poured into 1.5 L of methanol under stirring condition for precipitation. The precipitate was subsequently filtered, washed with deionized water and methanol and dried in vacuo.

^{1}H NMR spectrum was used to calculate the degree of substitution (DS) of carboxylate groups for hydroxyl groups in the glucose unit of α-1,3-glucan esters from the ratio of peak area of methyl protons ([CH_3]) in carboxylate group to that of ring protons in the glucose unit ([ring-H]), DS = ([CH_3]/3)/([ring-H]/7).

α-1,3-Glucan acetate (α-1,3-glucanAc). ^{1}H NMR (500 MHz, $CDCl_3$, *δ*, ppm): 2.10 (—CH_3), 4.07 (H-3, H-5, H-6), 4.65 (H-2), 5.05 (H-4), 5.20 (H-1).

α-1,3-Glucan propionate (α-1,3-glucanPr). ^{1}H NMR (500 MHz, $CDCl_3$, *δ*, ppm): 1.10 (—CH_3), 2.36 (—CH_2—), 4.05 (H-3, H-5, H-6), 4.59 (H-2), 5.02 (H-4), 5.20 (H-1).

α-1,3-Glucan butyrate (α-1,3-glucanBu). ^{1}H NMR (500 MHz, $CDCl_3$, *δ*, ppm): 0.93 (—CH_3), 1.62 (—$CH_2CH_2CH_3$), 2.11–2.32 (—$CH_2CH_2CH_3$), 4.02 (H-3, H-5, H-6), 4.63 (H-2), 5.04 (H-4), 5.15(H −1).

α-1,3-Glucan valerate (α-1,3-glucanVa). ^{1}H NMR (500 MHz, $CDCl_3$, *δ*, ppm): 0.91 (—CH_3), 1.33 (—$CH_2CH_2CH_2CH_3$), 1.56 (—$CH_2CH_2CH_2CH_3$), 2.13–2.33 (—$CH_2CH_2CH_2CH_3$), 4.02 (H-3, H-5, H-6), 4.64 (H-2), 5.05 (H-4), 5.13 (H-1).

α-1,3-Glucan hexanoate (α-1,3-glucanHe). ^{1}H NMR (500 MHz, $CDCl_3$, *δ*, ppm): 0.89 (—CH_3), 1.31 (—$CH_2CH_2CH_2CH_2CH_3$), 1.55 (—$CH_2CH_2CH_2CH_2CH_3$), 2.13–2.33 (—$CH_2CH_2CH_2CH_2CH_3$), 4.03 (H-3, H-5, H-6), 4.63 (H-2), 5.06 (H-4), 5.16 (H-1).

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