[SPECIAL EDITIONS on “NANO FIBER”–Transaction]

Simultaneous Nanofibrillation and Compounding of Wood Pulp Fibers Using Polyols as Plasticizers: Fabricating High-Performance Cellulose-Nanofiber-Reinforced Polyethylene Composites

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Abstract: As a reinforcing filler for polymer composite materials, cellulose nanofiber (CNF) is a promising alternative to conventional fillers from the viewpoints of its low cost, low density, biodegradability, high stiffness, and safety. A promising strategy for the preparation of CNF-reinforced polymer composite materials involves in-situ nanofibrillation, in which as-received wood pulp fibers are nanofibrillated into CNFs during the melt-compounding process. To further streamline this process, in this study, we used low-molecular-weight polyols, such as glycerol and glucitol, as nanofibrillation-assisting plasticizers, since polyols are expected to migrate and plasticize into the spaces between cellulose microfibrils in wood cell walls and break down the wood pulp fibers into CNFs. Never-dried needle-leaf bleached kraft pulp (NBKP), high-density polyethylene (HDPE), and a diblock copolymer (BCP), were used as the CNF resource, polymer matrix, and dispersant, respectively. The isolated cellulose fibers produced by the in situ process had diameters of between 200 and 500 nm. Furthermore, under the optimized conditions, the prepared composite material exhibited superior mechanical properties, with a Young's modulus and tensile strength of 3 GPa and 44 MPa, respectively, when produced with 10 wt% NBKP. These values correspond to a four-fold higher Young's modulus and a two-fold higher tensile strength than neat HDPE. Finally, the plasticization effects of glucitol and urea are compared and discussed from the viewpoints of the mechanical properties against the degree of nanofibrillation. This study provides a potential approach for an industrial-scale process.

(Received 2 October, 2019; Accepted 4 November, 2019)

1. INTRODUCTION

Cellulose-nanofiber-reinforced (CNF-reinforced) polymer composite materials are currently attracting high levels of attention because of the advantageous properties of CNF as a reinforcing filler [1–6], including its biocompatibility, low density, high aspect ratio, high Young's modulus (~140 GPa) [7–10], strength (~2 GPa) [11], optical transparency [12], and low thermal expansion [13]. A promising method for producing high-performance CNF-reinforced composites involves the in-situ nanofibrillation of as-received wood pulp fibers in a melting compounder. This approach is inspired by the successful preparation of nanoclay- and graphene-based nanocomposite materials [14,15], which are prepared

from macroscopic clay particles and graphite by melt-compounding processes, respectively. Yano and coworkers reported a pulp direct-kneading method, where surface esterified wood pulp fibers is subjected to nanofibrillation and compounding to yield dispersed CNFs in a high-density polyethylene (HDPE) matrix via melt compounding [16]. We also developed an efficient method for the preparation of CNF-reinforced HDPE composite materials from as-received wood pulp fibers, in which a nanofibrillation-assisting plasticizer (urea or a urea derivative) and a diblock copolymer (BCP) dispersant are used as additives [17]. Urea plays the role of a plasticizer for the wood-pulp fibers owing to its ability to weaken the hydrogen-bonding network between cellulose microfibrils. Importantly, the nanofibrillation-assisting

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plasticizer must be present in small amounts, not be a plasticizer for resin, and if feasible, be reactive toward cellulose in order for any remaining additive not to deteriorate the mechanical properties of the resulting composite. In fact, urea-accelerated in-situ nanofibrillation in an extruder produces less-fragmented CNF owing to both plasticization/nanofibrillation and reactions with the hydroxyl groups of cellulose fibers to form carbamates. Synergism with the BCP dispersant improves CNF dispersion and strengthens the CNF/HDPE interphase [18,19], which results in composite materials that exhibit significantly improved mechanical properties over those of neat HDPE, including a 6.9-fold increase in Young's modulus at a 10 wt% wood-pulp-fiber loading [17].

In this paper, we report another effective nanofibrillation-assisting plasticizer that provides high-performance CNF-reinforced HDPE composite materials. The new plasticizer is based on a low-molecular-weight polyol, such as glycerol or glucitol (Figure 1a and 1b). Polyols are well known to be effective plasticizers for hydroxyl-rich polymers, such as starch and poly(vinyl alcohol) (PVA) [20–22], with the formation of hydrogen bonds between the polyol and the hydroxyl-rich polymer considered to be crucial for plasticization [23]. Consequently, we hypothesized that a low-molecular-weight polyol can migrate and plasticize into the spaces between cellulose microfibrils in wood cell walls to break down wood pulp fibers into CNFs during melt compounding. Motivated by this idea, we investigated NBKP/HDPE/polyol/BCP composite materials in detail (Figure 1c; BCP = PDCPMA-*b*-PMTAI) and determined the optimum composition. Furthermore, we compare the effect of polyols with that of urea from the viewpoints of the mechanical properties against the degree of nanofibrillation.

Fig. 1 Chemical structures of (a) glycerol, (b) glucitol, and (c) PDCPMA-*b*-PMTAI.

2. EXPERIMENTAL

2.1 Materials

Never-dried needle-leaf bleached kraft pulp (NBKP) (18 wt%) was supplied by Daio Paper Corp. (Tokyo, Japan). The pulp was mechanically refined using a Niagara Beater until the value of its Canadian Standard freeness was below 150 mL. Two samples of HDPE were used; a sample referred to as “HE-3040” purchased from the Sumitomo Seika Chemicals Co., Ltd. (Osaka, Japan) in the form of fine particles (diameter $\sim 11 \mu\text{m}$), and another referred to as “Suntec HD J-320” purchased from Asahi Kasei Corp. (Tokyo, Japan) in the form of pellets. The poly(dicyclopentenylmethoxyethyl methacrylate)-*block*-poly[2-(methacryloyloxy)ethyltrimethylammonium iodide] (PDCPMA-*b*-PMTAI) polymer dispersant was synthesized as described previously [17]. Glycerol (99 %) and glucitol (97 %) were purchased from Nacalai Tesque (Kyoto, Japan). All other chemicals were obtained from commercial sources and used without further purification.

2.2 Compounding and Injection Molding

CNF-reinforced HDPE composites were prepared according to a previously reported procedure [17], with the exception that glycerol or glucitol was instead of urea or a urea derivative. In brief, never-dried refined NBKP (10 g absolute dry mass) and HE-3040 were mixed into a pulp slurry in a predetermined weight ratio. In experiments where the effect of the polymer dispersant was investigated, 20 wt% PDCPMA-*b*-PMTAI dissolved in a 1:2 (v/v) 2-propanol/water mixture was added to the pulp slurry. The mixture was dried at 105 °C overnight to yield a dry sample referred to as the “premix.” The typical concentration of NBKP in the premix was 30 wt%. The premix was diluted with J-320 and mixed with glycerol or glucitol at a predetermined weight ratio, leading to 10 wt% of NBKP. The mixture was kneaded with a twin-screw miniextruder (Xplore MC 15, 15 mL total volume, Xplore Instruments BV, Netherlands), with kneading performed at 140 °C for the predetermined time (mostly 60 min) at a screw speed of 200 rpm under a flow of inert nitrogen. The molten mixture was extruded directly into a micro-injection molder (Xplore IM 12, 12 mL total volume, Xplore Instruments BV) and injected into the mold (1200202, ISO 527-2/1BA standard, Xplore) to yield dumbbell-shaped test pieces that were 40 mm long $\times$ 2 mm thick $\times$ 5 mm wide (at the narrowest point). The

injection and mold die temperatures were set to 150 and 50 °C, respectively, and an injection pressure of 10 bar was used for 5 s, after which it increased to 13 bar for 32 s.

2.3 Mechanical Properties

The tensile strengths and moduli of the samples were measured using a universal mechanical testing machine (Tensilon RTG-1310, A&D Co., Tokyo, Japan). A cell load and crosshead speed of 1 kN (UR-1 KN-D, A&D) and 10 mm min⁻¹ were used, respectively. Tensile deformation was monitored by a non-contact video extensometer (TRView X, Shimadzu Co., Kyoto, Japan). The average values of Young's modulus, tensile strength, elongation at break, and work of fracture were calculated with their standard deviations taken as errors. The work of fracture corresponds to the area below the stress-strain curve. All samples were dried at rt overnight prior to mechanical testing.

2.4 Characterizing Morphologies

Polarized optical microscopy (POM) images were recorded on a BX 60 microscope (Olympus Corp., Tokyo, Japan) for dumbbell-shaped specimens that were cut using a microtome (REM-710, Yamato Kohki Co., Saitama, Japan) to thicknesses of ~20 µm in the machine direction. The slice was placed between two quartz plates and heated using a Linkam 10002 hot stage (Linkam Scientific Instruments, Ltd., UK) at 140 °C. To count the individual un-nanofibrillated pulp fibers, each color image (1296 × 923 pixels) was

converted to grayscale and the total fiber area (A) was calculated using Image-J software (<https://imagej.nih.gov>). In this paper, the degree of pulp-fiber nanofibrillation (%) is defined to be: $100 \times (1 - A_1/A_0)$, where A_1/A_0 is the ratio of the un-nanofibrillated-fiber area in the composite against the area of the reference 10:90 (w/w) NBKP/HDPE composite prepared over a short kneading time (5 min). Field-emission scanning electron microscopy (FE-SEM) was performed using a JEOL JSM-6700 F microscope operating at 1.5 kV. The dumbbell-shaped test samples were extracted with boiling xylene (155 °C) for 3 h, successively washed with toluene, and then dried under vacuum at 100 °C overnight, resulting in residual cellulosic sheets. Each sample was sputter-coated with a thin layer of gold-palladium to enhance its conductivity (Hitachi Ion Sputter E-1010) prior to SEM.

3. RESULTS AND DISCUSSION

3.1 Preparing Composite Materials Using Polyols

The composite materials were firstly prepared from the mixtures of NBKP, HDPE, and a plasticizer using the method described in our previous paper, with the exception that a polyol (glycerol or glucitol) was used instead of urea or a urea derivative [17]. The amount of polyol and kneading time were optimized from the viewpoints of degree of nanofibrillation, mechanical properties, and the microscopic structures

Fig. 2 Representative FE-SEM images of (a) original refined NBKP, (b) xylene-extracted 10:87:3 (w/w/w) NBKP/HDPE/glycerol (sample 4), (c) 10:87:3 (w/w/w) NBKP/HDPE/glucitol (sample 9), and (d) 10:83:3:4 (w/w/w/w) NBKP/HDPE/glucitol/PDCPMA-*b*-PMT AI (sample 18).

of the fibrillated pulp fibers. Subsequently, the effect of the polymer dispersant was investigated in the section 3.2. The disintegration of NBKP into CNF was confirmed by SEM observation of the xylene-extracted HDPE composites (Figure 2). These images of the isolated fibers show downsized submicron fibers with rather uniform thickness and diameter, indicating successful nanofibrillation of NBKP during melt-compounding process with a plasticizer.

3.1.1 Effects of Glycerol and Glucitol Concentrations

Table 1 lists the degrees of nanofibrillation, Young's moduli, tensile strengths, elongations at break, and work-of-fracture energies of the HDPE/NBKP/plasticizer (glycerol or glucitol) composite materials prepared by melt compounding. Figure 3 also shows the relationships between the plasticizer concentration and Young's modulus, tensile strength, and degree of nanofibrillation. The degree of nanofibrillation was observed to increase with increasing plasticizer concentration; however, the degree of nanofibrillation was almost constant, at around 70 %, when the concentration of each plasticizer exceeded 3 wt%, with glucitol yielding slightly higher degrees of nanofibrillation than glycerol. All composites exhibited Young's moduli and tensile strengths that were better than those of neat

HDPE ($E = 0.75$ GPa, $\sigma = 22.6$ MPa) [17].

Excess amounts of plasticizer may adversely affect mechanical properties. For example, when glycerol was used as the plasticizer, the Young's modulus and tensile strength of the composite first increased to a concentration of 2 wt% due to the plasticization of NBKP, and then decreased gradually as the concentration was further increased. On the other hand, glucitol was increasingly mechanically reinforcing the composites as the concentration increased to 3 wt%, after which the Young's modulus appeared to plateau at around 1.8 GPa. The difference between glycerol and glucitol may be related to the melting point (T_m). Glycerol is a liquid at room temperature ($T_m = 18$ °C), whereas glucitol is a solid ($T_m = 95$ °C), which suggests that glucitol impacts plasticization of the composites less because of its high T_m . Hence, we focused on glucitol-based composite materials in the following sections.

3.1.2 Effect of Kneading Time

Table 2 and Figure 4a show how kneading time is related to the degree of nanofibrillation and the mechanical properties of the 10:87:3 (w/w/w) NBKP/HDPE/glucitol composite. As expected, the degree of nanofibrillation was observed to increase with kneading time. On the other hand, mechanical

Table 1 Tensile properties of NBKP/HDPE composites prepared with glycerol or glucitol as a plasticizer.^a

Sample	plasticizer	Loading (wt%)	Degree of nanofibrillation ^b (%)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Work of fracture (MJ m ⁻³)
1	-	-	41 ± 3	1.18 ± 0.05	27 ± 0.12	17 ± 0.21	3.9 ± 0.05
2	glycerol	1	62 ± 1	1.52 ± 0.13	32 ± 0.13	9.2 ± 0.46	2.4 ± 0.11
3	glycerol	2	59 ± 5	1.65 ± 0.12	37 ± 0.31	7.4 ± 0.30	2.1 ± 0.08
4	glycerol	3	69 ± 4	1.53 ± 0.20	39 ± 0.19	6.5 ± 0.08	1.8 ± 0.02
5	glycerol	4	68 ± 1	1.36 ± 0.02	38 ± 0.06	6.5 ± 0.14	1.7 ± 0.06
6	glycerol	5	69 ± 3	1.06 ± 0.03	31 ± 0.37	9.1 ± 0.73	2.1 ± 0.18
7	glucitol	1	66 ± 1	1.43 ± 0.05	30 ± 0.07	11 ± 0.15	2.7 ± 0.04
8	glucitol	2	64 ± 7	1.75 ± 0.08	35 ± 0.15	8.3 ± 0.12	2.4 ± 0.03
9	glucitol	3	75 ± 2	1.71 ± 0.08	39 ± 0.18	6.8 ± 0.42	2.0 ± 0.13
10	glucitol	4	76 ± 2	1.83 ± 0.09	42 ± 0.27	6.0 ± 0.07	1.9 ± 0.05
11	glucitol	5	77 ± 3	1.80 ± 0.06	43 ± 0.23	6.0 ± 0.15	1.9 ± 0.06

^aNBKP loading: 10 wt%; kneading time: 60 min. ^bSee Experimental section 2.4 for details.

Fig. 3 (a, c) Representative stress-strain curves for NBKP/HDPE/plasticizer composites with various plasticizer concentrations: a, glycerol (Gly) and c, glucitol (Glu). (b, d) Young's modulus (blue), tensile strength (red), and degree of nanofibrillation (green) as functions of plasticizer content: b, glycerol; d, glucitol.

properties, especially the Young's modulus, were largely unaffected by kneading time. We previously reported that CNF dispersion mainly increases tensile strength, since strength is affected by defects in the composite [18]. On the other hand, the Young's modulus is related to interfacial strength [18]; consequently, the limited increase in Young's modulus observed in the present case is ascribable to similar interfacial strengths among samples 9 and 12–16. This means that glucitol itself cannot reinforce the

interphase between CNF and HDPE effectively. Interestingly, the mechanical properties of the NBKP/HDPE composite prepared without glucitol (Figure 4b) was almost unaffected by kneading time, despite the degree of nanofibrillation gradually increasing with kneading time. This observation is ascribable to severe fragmentation during kneading due to the absence of glucitol.

Figure 5 shows SEM images of cellulose fibers isolated from samples 9 and 12–16 through extraction

Table 2 Effect of kneading time on the tensile properties of the 10:87:3 (w/w/w) NBKP/HDPE/glucitol composite.

Sample	Kneading time (min)	Degree of nanofibrillation ^a (%)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Work of fracture (MJ m ⁻³)
12	5	13 ± 1	1.48 ± 0.12	32 ± 0.21	7.2 ± 0.21	1.8 ± 0.10
13	10	21 ± 6	1.50 ± 0.13	33 ± 0.25	7.7 ± 0.32	2.0 ± 0.08
14	15	34 ± 8	1.73 ± 0.22	35 ± 0.28	6.8 ± 0.10	1.8 ± 0.03
15	30	53 ± 6	1.88 ± 0.31	37 ± 0.20	6.3 ± 0.38	1.8 ± 0.08
16	45	58 ± 7	1.71 ± 0.05	39 ± 0.13	6.4 ± 0.10	1.9 ± 0.02
9	60	75 ± 2	1.71 ± 0.08	39 ± 0.18	6.8 ± 0.42	2.0 ± 0.13

^aSee Experimental section 2.4 for details.

Fig. 4 Young's modulus (blue), tensile strength (red), and degree of nanofibrillation (green) as functions of kneading time: (a) the 10:87:3 (w/w/w) NBKP/HDPE/glucitol composite and (b) the 10:90 (w/w) NBKP/HDPE composite.

of the HDPE matrix with boiling xylene, which reveals disintegration of the original NBKP with $\sim 10\text{-}\mu\text{m}$ -diameter [17] into thin fibers with thicknesses and diameters that become rather uniform with increasing kneading time. Figure 6 shows magnified SEM images of isolated cellulose fibers from sample 9, with diameters of 200–500 nm. The observed morphology indicates that CNFs were successfully produced during glucitol-assisted melt processing.

3.2 Effect of the Polymer Dispersant

A block-copolymer-type (BCP-type) dispersant has previously been reported to facilitate good CNF dispersion in apolar HDPE [18,19]. Furthermore, the PDCPMA-*b*-PMTAI BCP spontaneously adsorbs onto the CNF surface produced by melt compounding during in situ nanofibrillation, leading to excellent mechanical properties owing to the well dispersed CNFs in the HDPE and the increase in interphase strength [17]. Hence, in this study, we tested the

NBKP/HDPE/glucitol/PDCPMA-*b*-PMTAI mixture and optimized the PDCPMA-*b*-PMTAI loading (Table 3 and Figure 7). The optimal composition was found to be 10:83:3:4: the Young's modulus and tensile strength of the composite were highest, at 3 GPa and 44 MPa,

Fig. 6 FE-SEM image of isolated cellulose fibers of the xylene-etched 10:87:3 (w/w/w) NBKP/HDPE/glucitol composite (sample 9).

Fig. 5 FE-SEM images of xylene-etched 10:87:3 (w/w/w) NBKP/HDPE/glucitol composites prepared by kneading for: (a) 5 min (sample 12), (b) 10 min (sample 13), (c) 15 min (sample 14), (d) 30 min (sample 15), (e) 45 min (sample 16), and (f) 60 min (sample 9).

Fig. 7 (a) Representative stress-strain curves for the 10:87-*x*:3:*x* (w/w/w/w) NBKP/HDPE/glucitol/PDCPMA-*b*-PMATI composite with various BCP contents. (b) Young's modulus (blue), tensile strength (red), and degree of nanofibrillation (green) as functions of BCP loading.

respectively, which corresponds to a four-fold higher Young's modulus and a two-fold higher tensile strength than those of neat HDPE ($E = 0.75$ GPa, $\sigma = 22.6$ MPa). The Young's modulus (3 GPa) was close to that predicted (3.6 GPa) on the basis of Halpin-Tsai composite theory [18]. This suggests that the produced CNFs were not damaged by the present compounding condition.

3.3 Comparing Glucitol with Urea

We previously reported that urea is an effective plasticizer for the in-situ nanofibrillation of wood pulp fibers. Urea plays a crucial role in producing less-fragmented CNF during the melt-compounding step; for example, the optimized 10:80:4:6 (w/w/w/w) NBKP/HDPE/urea/PDCPMA-*b*-PMATI composite exhibited a Young's modulus of 5.2 GPa and a tensile strength of 58 MPa [17]. Two mechanisms that operate in synergy were proposed for the urea-based plasticizer. One involves surface reactions between the urea-derived cyanic acid (HNCO) and the hydroxyl groups of cellulose to form carbamate ($-O-(C=O)-NH_2$) functionalities that strengthen the CNF/HDPE-matrix interphase (the carbamate effect). The

second involves nanofibrillation, in which the native or HNCO-reacted cellulose is broken down into nanofibers (the nanofiber effect). On the other hand, the glucitol-based plasticizer only accelerates nanofiber formation, expecting single mechanism of the nanofiber effect.

To compare these effects, Figure 8 summarizes relative Young's modulus (E_C/E_M) and tensile strength (σ_C/σ_M) against the degree of nanofibrillation, where the subscripts C and M represent the values for the composite and matrix (neat HDPE), respectively. It should be noted that the degree of nanofibrillation for the urea-based plasticizer [17] was renewed according to the definition of the degree of nanofibrillation in this study (see Experimental Section 2.4). For the urea-based composites, the E_C/E_M value increased linearly as the degree of nanofibrillation increased owing to both the carbamate and nanofiber effects (see Figure 8a, arrow A). The addition of the BCP yielded slight increase in E_C/E_M due to the dispersion effect (arrow B). On the contrary, the E_C/E_M for the glucitol-based composites remained constant unless the BCP was added (arrow C), resulting from the less

Table 3 Effect of PDCPMA-*b*-PMTAI (BCP) loading on the properties of the NBKP/HDPE/glucitol composite.^a

Sample	BCP loading (%)	Degree of nanofibrillation ^b (%)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Work of fracture (MJ m ⁻³)
9	0	75 ± 2	1.71 ± 0.08	39 ± 0.18	6.8 ± 0.42	2.0 ± 0.13
17	2	77 ± 5	2.23 ± 0.11	44 ± 0.71	4.8 ± 0.17	1.5 ± 0.07
18	4	81 ± 1	3.00 ± 0.19	44 ± 0.30	3.6 ± 0.05	1.1 ± 0.02
19	6	80 ± 7	2.64 ± 0.40	42 ± 0.23	3.5 ± 0.31	1.0 ± 0.08

^a NBKP/HDPE/glucitol/PDCPMA-*b*-PMTAI = 10:87-*x*:3:*x* (w/w/w/w; *x* = BCP loading); kneading time: 60 min. ^bSee Experimental section 2.4 for further details.

Fig. 8 Summary of (a) relative Young's modulus and (b) tensile strength of the glucitol-based (red) and urea-based (blue) composite materials against degree of nanofibrillation under different compounding conditions: (closed circles) plasticizer concentrations; (open circles) kneading time; (triangles) addition of BCP.

impact of the nanofibrillation for the Young's modulus, as mentioned in the section 3.1.2. Upon the addition of BCP, the E_C/E_M significantly increased (arrow D). Basically, a BCP dispersant has two main effects, that is, dispersion of CNF in a matrix [19] and improvement of interphase strength [18]. Considering the degree of nanofibrillation increased slightly and thus the dispersion effect was less dominant, the interfacial effect of BCP brought about a remarkable increase in the Young's modulus of the glucitol-based composites, as marked contrast to the urea-based ones.

Similar to E_C/E_M , the σ_C/σ_M values were dependent on the degree of the nanofibrillation (Figure 8b). Tensile strength is basically related to the dispersion of CNF [18]. Though the degree of nanofibrillation for both the glucitol and urea-based composites were almost the same at their highest σ_C/σ_M value, these values were different. This reason has not been understood well, but the difference of σ_C/σ_M between the glucitol- and urea-based composites would be related to that of E_C/E_M .

4. CONCLUSIONS

We developed an effective method for the preparation of CNF-reinforced HDPE composite materials. NBKP was used as the CNF raw material, and a polyol (glycerol or glucitol) was used as the plasticizer during melt compounding. The NBKP, HDPE, and polyol mixture was kneaded to produce CNFs in the HDPE matrix. Glucitol was found to be a better plasticizer than glycerol. The addition of the PDCPMA-*b*-PMATI polymer dispersant resulted in

superior mechanical properties owing to the improvement of the interphase strength. The optimized composite material produced in this study exhibited satisfactory mechanical properties, namely a four-fold higher Young's modulus and two-fold higher tensile strength than neat HDPE. Since the in-situ nanofibrillation method in this study provides a short and practical preparation route, it is possibly one of the best methods for the large-scale industrial preparation of CNF-reinforced polymer composite materials.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This research was supported by grants from projects of the National Agriculture and Food Research Organization (NARO) Bio-oriented Technology Research Advancement Institution (integration research for agriculture and interdisciplinary field) and JSPS KAKENHI (Grant Number 17H06238).

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