Development and Characterization of Food-Grade Tracers for the Global Grain Tracing and Recall System

KYUNG-MIN LEE,[†] PAUL R. ARMSTRONG,[‡] J. ALEX THOMASSON,[§] RUIXIU SUI,[#] MARK CASADA,[‡] AND TIMOTHY J. HERRMAN*,[†]

[†]Office of the Texas State Chemist, Texas Agricultural Experiment Station, College Station, Texas 77841, [‡]Center for Grain and Animal Health Research, Agricultural Research Service, U.S. Department of Agriculture, Manhattan, Kansas 66502, [§]Biological and Agricultural Engineering Department, Texas A&M University, College Station, Texas 77843, and [#]Cotton Ginning Research Unit, Agricultural Research Service, U.S. Department of Agriculture, Stoneville, Mississippi 38776

Tracing grain from the farm to its final processing destination as it moves through multiple grain-handling systems, storage bins, and bulk carriers presents numerous challenges to existing record-keeping systems. This study examines the suitability of coded caplets to trace grain, in particular, to evaluate methodology to test tracers' ability to withstand the rigors of a commercial grain handling and storage systems as defined by physical properties using measurement technology commonly applied to assess grain hardness and end-use properties. Three types of tracers to dispense into bulk grains for tracing the grain back to its field of origin were developed using three food-grade substances [processed sugar, pregelatinized starch, and silicified microcrystalline cellulose (SMCC)] as a major component in formulations. Due to a different functionality of formulations, the manufacturing process conditions varied for each tracer type, resulting in unique variations in surface roughness, weight, dimensions, and physical and spectroscopic properties before and after coating. The applied two types of coating [pregelatinized starch and hydroxypropylmethylcellulose (HPMC)] using an aqueous coating system containing appropriate plasticizers showed uniform coverage and clear coating. Coating appeared to act as a barrier against moisture penetration, to protect against mechanical damage of the surface of the tracers, and to improve the mechanical strength of tracers. The results of analysis of variance (ANOVA) tests showed the type of tracer, coating material, conditioning time, and a theoretical weight gain significantly influenced the morphological and physical properties of tracers. Optimization of these factors needs to be pursued to produce desirable tracers with consistent quality and performance when they flow with bulk grains throughout the grain marketing channels.

KEYWORDS: Traceability; grain; recall; safety; tracer

INTRODUCTION

Section 306 of the Bioterror Act of 2002 (*1*) administered by the U.S. Food and Drug Administration requires grain traceability one step forward and backward (*2*). For a commercial grain storage facility serving as the first collection point, tracing grain back to the farm(s) origin and forward to a terminal grain elevator or processor is required. The EU General Food Traceability Regulation (EC/178/2002) (*3*) requires labeling and traceability for food and feed, including biotech grains and grain products, and identifying immediate suppliers or customers of the product. The International Standards Organization (ISO) offered a new food safety standard (*4*) on traceability in the feed and food chain to provide general principles and requirements for the design and implantation of a feed and food traceability system. A traceability system that enables rapid identification of the market pathway will reduce business risk, improve product safety, and lower costs for recall and liability (*5, 6*).

Grain loaded onto a truck at the field is hauled to farm storages, country elevators, or inland subterminals (*7, 8*). Grain shipped to commercial grain storage facilities is frequently commingled with grain from other farms. Export terminal and large processing facility elevators contain commingled grains delivered from many geographical regions in the United States from possibly thousands of farms, which greatly increases the challenge of tracing grain to its point of origin. Competitive or complementary transportation modes and their paths in moving grains between the original and final destinations are determined by transportation accessibility, costs per mile, local requirement, and efficiency (*7*). Truck transportation remains the most flexible in times and delivery routes and is the dominating transportation mode for a short haul of grains. Rail and barge transportation is preferred over trucks for a longer haul distance, handling a large amount of grains (*7, 9*).

*Corresponding author [phone (979) 845-1121; fax (979) 845-1389; e-mail tjh@otsc.tamu.edu].

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Low cost and easy application to the current grain transportation and processing system in most countries would surely be one advantage of the proposed coded caplet traceability system over the existing traceability systems. Even their traceability efficiency may be improved by properly merging the part of procedures and technologies obtained from the coded caplet traceability system. Using information recorded on a coded caplet and accompanying database, system participants and users can identify grain origin, movement, and quality traits even after grains are commingled and shipped to multiple distributors.

Pharmaceutical caplets are typically manufactured via a four-stage process: dispensing, granulation, compression, and packing. The granulation process can be classified into five different methods: wet granulation, dry granulation, direct compression, fluid bed granulation, and spray-dried granulation (*10*). In a direct compression method, caplets are manufactured simply by compressing the mixture of active ingredients and excipients without blending the powders prepared by the wet and dry granulation. This method is simple, speedy, and the most advanced, and it requires less labor and processing time. Due to these advantages, the direct compression method was used in this study for tracer production. A caplet coating using poured or sprayed coating materials (e.g., shellac, polymers, and sucrose-based syrup) in a coating pan helps keep the physical shape of a caplet from body fluids, protects the stomach lining, and helps control release of the caplet ingredients (*11*). In this traceability system, a coating process is necessary to maintain the caplet shape and protect the marked codes on the surface of a tracer. There are different ways of marking a pharmaceutical caplet: printing with ink, embossing, debossing, and engraving (*11*, *12*). The proposed coded traceability system was initially planned to apply the edible ink for imprinting tracers before or after coating.

The objectives of this study were to develop different types of tracers using nonadulterant food-grade materials for the grain and characterize the morphological, physical, and spectroscopic properties of uncoated and coated tracers prior to printing ID marking with a code or numerals to identify the origin of grains at any point in the grain supply chain, enabling trace back to the origin of fields. Particularly, the spectroscopic property and spectral data processing technique were explored as tools to substitute time-consuming and destructive measurements for tracer quality and improve the system efficiency. The characterization of tracers' morphological, physical, and spectroscopic properties before and after coating should provide scientific criteria and guidelines to produce a tracer and coating solution most suitable for this proposed traceability system. On the basis of these criteria, research advances in developing tracer technology based on desirable physicochemical properties and moisture resistant tracers will improve final tracer quality and performance in bulk grain during handling and commercial storage conditions.

MATERIALS AND METHODS

Materials. Direct compressible formulations for three types of tracers, sucrose-, starch-, and cellulose-based tracers, were made of processed sugar (Di-Pac Direct Compacting & Tableting Sugar, Domino Foods, Inc., Baltimore, MD), pregelatinized starch (C*PharmaGel DC 93000, Cargill, Inc., The Netherlands), silicified microcrystalline cellulose (Prosolv 50, Penwest Pharmaceuticals Co., Patterson, NY), and magnesium stearate (TABLETpress.NET, Athens, OH). All of the materials are food-grade substances and free from food allergens caused by grain proteins. Tracers were coated with two coating materials using an aqueous coating system: pregelatinized starch (INSTANT PURE-COTE, Grain Processing Corp., Muscatine, IA) and hydroxypropylmethylcellulose (HPMC) (Methocel K4M, Dow Chemical Co., Midland, MI). A tracer film coating helps improve tracer visual appearance and minimize mechanical damage and abrasions of the tracer and surface-printed ID code.

Table 1. Direct Compressible Formulations for Three Different Types of Tracers

ingredient	sucrose-based tracer	starch-based tracer	cellulose-based tracer
processed sugar	97.0		35.0
pregelatinized starch		100.0	
SMCC[a]			64.5
magnesium stearate	3.0		0.5

[a] SMCC, silicified microcrystalline cellulose.

Table 2. Composition of Aqueous Coating Solutions

coating solution	composition (% w/w)
pregelatinized starch	pregelatinized starch (15), glycerol (2), water (83)
HPMC[a]	HPMC (5), triethyl citrate (1), water (94)

[a] HPMC, hydroxypropylmethylcellulose.

Table 3. Coating Process Conditions Used for Tracer Coating with Different Coating Solutions to Yield 1, 2, and 3% Weight Gain Tracers

parameter	pregelatinized starch	HPMC[a]
pump rate of coating solution (g/min)	4.5	11
applied solution amount (g)		
1% weight gain	60	180
2% weight gain	120	360
3% weight gain	180	540
spray air pressure (kPa)	96.5	93.1
air flow rate (L/s)	25.5	26.4
pan speed (rpm)	25	25
inlet temperature (°C)	53	68
outlet air temperature (°C)	41	44

[a] HPMC, hydroxypropylmethylcellulose.

Tracer Preparation. The ingredients of sucrose-, starch-, and cellulose-based tracers were added to a V-type mixer according to the ratios presented in **Table 1** and thoroughly mixed for 60 min. The premixed formulation was then loaded into an auxiliary hopper in a tablet press (FSP-30 Single Punch Tablet Press, Minhua, Shanghai, China). The pressure exerted on the tracer was adjusted for similar tracer hardness among three types of tracers using the guide-bar by considering the binding force between particles in the formulation powder. The production rate (the number of tracers produced per minute) also needed to be optimized to avoid variation in caplet quality and ranged between 45 and 50 tracers/min. The tracer-forming die with dimensions of 11 mm length × 6 mm width × 4 mm height was designed for the tablet press. The tracer weight and dimension were frequently checked for consistent tracer quality during production. The manufactured tracers were placed in double airtight plastic bags at room temperature before coating.

Coating Processing. Two types of aqueous coating solutions were prepared by mixing different polymers and plasticizers with distilled water (**Table 2**) at ambient temperature for 20 min. A 900 g batch of uncoated tracers was loaded to a laboratory-scale pan coater (Hi-Coater, Vector Corp., Marion, IA) for coating. For application of coating solution, coating process parameters were effectively controlled while the amounts of applied coating solutions were varied to obtain theoretical coating weight gains of 1, 2, and 3% (**Table 3**). Coating times and the applied solution amount varied to achieve desirable weight gains because the coating solutions had different solid concentrations and the tracer volume per batch was associated with a tracer density. Coated tracers were kept at room temperature before morphological, physical, and spectroscopic properties were evaluated.

Tracer Morphological and Physical Properties. Individual weights of 100 tracers for each type of uncoated and coated tracers were weighed and averaged using an analytical balance (Aldinger, Dallas, TX). The thickness, length, and width of 25 randomly selected uncoated and coated tracers were measured using a digital micrometer (**Figure 1**). The difference of the averaged measurements on coated and their corresponding uncoated tracers was considered as the amount of coating material
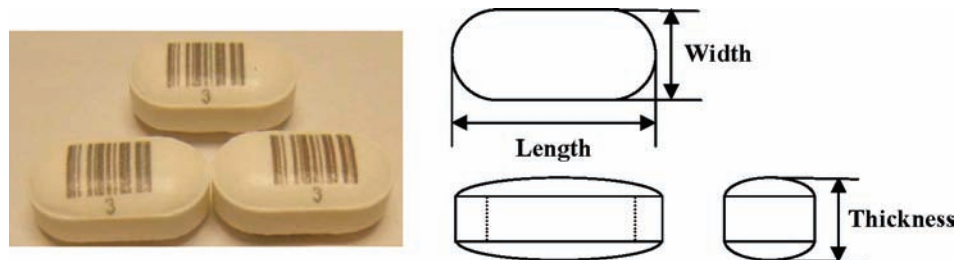
Figure 1. Bar-coded tracer and tracer dimension.

deposited on their surface (coating film thickness). For density measurement of tracers, the tracer pellet lot was first divided using a Boerner divider (Seedburo Equipment Co., Chicago, IL). Four representative samples were obtained from each lot with the divider. Each sample was used to fill a multipycnometer cup leaving $^1/_{16}$ to $^1/_8$ in. of space on top. Particle density was then measured using a helium-gas multipycnometer (model MVP-1, Quantachrome Corp., Syosset, NY). Moisture adsorption rates of tracers were quantified by weighing approximately 10 g of tracers, placing them into mesh bags, and allowing them to adsorb moisture in an environmental chamber maintained at 80% RH and 20.5 °C. Tracers were exposed to these conditions for 0, 4, 24, and 48 h. Moisture content was then determined using ASABE Standards (*13*) for wheat. Triplicate measurements were made, and average moisture was reported. This method was also used to condition tracers for the subsequent physical tests described below. Shear strength was determined by placing tracers in a shear box designed to shear tracers transverse to the long axis of the tracer. Shearing was in the direction of the shorter cross-sectional dimension designated as width in **Figure 1**. A stepper motor attached to a load cell provided deformation and force measurements. A personal computer (PC) was used to control the motor and sense load cell force measurements. The deformation rate was 2.5 mm/s. Five tracers were tested for each moisture conditioning period and average results reported. Compression strength of the tracers was performed using the same PC, stepper motor, and load cell apparatus. Tracers were placed on a horizontal platform with the width of the tracer oriented vertically. Loading was essentially between parallel plates. The tracer was loaded until failure and the peak force recorded. Five tracers were tested for each moisture conditioning period and average results reported. Tracer abrasion resistance was tested using a tangential abrasive dehulling device (TADD) (Venables Machine Works Ltd., Saskatoon, SK, Canada). Approximately 10 g of tracers was weighed and then ground in the TADD for 10 s, removed, weighed, and reground for an additional 10 s. Weights prior to grinding and after 10 and 20 s of grinding were recorded as measures of abrasive resistance. Two replicates were done for each conditioning period and average results reported. Weights were normalized to the original weight of the sample for easier comparison. Normalized weight is thus the decimal percentage of material remaining after each grind.

Raman Spectroscopy. Raman spectra for ingredient powders and manufactured tracers were recorded on RamanStation 400F (Perkin-Elmer, Beaconsfield, Buckinghamshire, U.K.) interfaced with Spectrum (v. 6.3) software in the Raman shift range from 200 to 3500 cm^{-1} using a near-infrared laser light source of 785 nm at 350 mW and a 256 × 1024 pixel CCD detector. The powder and tracer samples were placed on the well plate, and their Raman spectra were collected at a resolution of 8 cm^{-1} from the large sample spot consisting of six locations around the centered location with exposure times of 1 sec and 10 scans at the sample location. The spectra from seven locations were co-added to give a single spectral file. Ten samples selected from different types of ingredient powders and tracers were analyzed for this study. During the spectra measurements, the powder and tracer samples were stored in screw-capped glass bottles at room temperature. Prior to the spectral analysis, the collected spectra were baseline corrected and normalized to reduce variation in Raman signal due to subtle changes in experimental conditions. Multivariate statistical techniques such as principal component analysis (PCA) and cluster analysis were performed for spectral data reduction and tracer classification.

Statistical Analysis. A four-factor factorial design was employed in this study. The effect of four factors, including the type of tracer, coating material, a theoretical weight gain, and conditioning period, was

Table 4. Four Factors in the Factorial Design

factor	type and level
type of tracer (3)	sucrose-based tracer
	starch-based tracer
	cellulose-based tracer
coating material (2)	pregelatinized starch
	HPMC[a]
theoretical weight gain (3)	1, 2, and 3%
conditioning period (4)	0, 4, 24, and 48 h

[a] HPMC, hydroxypropylmethylcellulose.

investigated on the morphological and physical properties (weight, dimension, moisture content, peak compression force, peak shear force, and TADD abrasion) of uncoated and coated tracers (**Table 4**). General linear model analysis using the SAS Proc GLM procedure was used to determine the effect of the four factors. The means of the morphological and physical properties of tracers were compared using least significant difference (LSD) and least-squares means (LSMeans) using the PDIFF option. All statistical analysis was conducted by SAS software (*14*).

RESULTS AND DISCUSSION

Properties of Raw Materials. Three food-grade substances were used for manufacturing tracers with a single punch tablet press because they have suitable binding property, flowability, and compressibility in direct compression formulations. Sucrose used for a sucrose-based tracer is a processed sugar powder with dextrin, the flowability and compressibility of which are desirable for a direct compression method involving a tablet press. This sucrose powder contains many hydroxyl groups of chains that most likely react with water molecules under certain atmospheric conditions. Starch used for starch-based tracers is partially pregelatinized maize starch without allergens requiring labeling by the European Food Labeling Directive 2000/13/EC (*15*) and the U.S. Food Allergen Labeling and Consumer Protection Act (FALCPA) of 2004 (*16*). This pregelatinized starch possesses a high binding capacity, low friability, and good compressibility and flowability without a lubricant, resulting in acceptable tracer hardness. The degree of starch gelatinization affects the crystallinity of the starch molecule so that it may modify the physical, structural, and hygroscopic properties of powder, tracer, and coating formation on a starch-based tracer (*17, 18*). Microcrystalline cellulose (MCC) has been used as a filler and binder in pharmaceutical tabletting, but it has a problem in the compression property, that is, much lower tensile strength after wet granulation (*19*). Contrarily, despite its similar structure to that of MCC (*20*), silicified microcrystalline cellulose (SMCC) used for a cellulose-based tracer has an ability to retain compaction properties after wet and dry granulation. In addition, SMCC has other beneficiary characteristics with respect to mechanical properties over conventional MCC (*19*).

Tracer Manufacturing. A direct compression method involving a tablet press appeared to be ideal for producing a tracer because the production of tracer was simple, fast, and economical while

Table 5. Analysis of Variance (ANOVA) for Moisture Content and Physical Properties of Coated Tracers[a]

source[b]	MC		compression		shear		TADD20	
	F value	P value	F value	P value	F value	P value	F value	P value
coat	**207.1**	**<0.0001**[c]	**34.9**	**<0.0001**	**104.1**	**<0.0001**	**190.4**	**<0.0001**
CON	**21612.7**	**<0.0001**	**550.3**	**<0.0001**	**168.1**	**<0.0001**	**104.6**	**<0.0001**
coat × CON	**365.4**	**<0.0001**	**7.9**	**0.0013**	3.3	0.0211	**6.7**	**0.0004**
tracer	**369913.0**	**<0.0001**	**251.2**	**<0.0001**	**1617.2**	**<0.0001**	**573.6**	**<0.0001**
coat × tracer	**471.0**	**<0.0001**	2.5	0.0870	**27.0**	**<0.0001**	**51.9**	**<0.0001**
CON × tracer	**3982.1**	**<0.0001**	**53.8**	**<0.0001**	**32.3**	**<0.0001**	**17.0**	**<0.0001**
coat × CON × tracer	**140.2**	**<0.0001**	1.3	0.2436	1.4	0.2049	3.2	0.0068
WG	**70.4**	**<0.0001**	**8.2**	**0.0004**	**122.5**	**<0.0001**	**17.5**	**<0.0001**
coat × WG	0.6	0.5638	**5.6**	**0.0045**	**23.1**	**<0.0001**	6.3	0.0028
CON × WG	3.2	0.0058	0.8	0.5845	2.2	0.0424	0.8	0.5766
coat × CON × WG	**14.5**	**<0.0001**	1.8	0.0979	1.6	0.1479	0.9	0.5221
tracer × WG	**33.7**	**<0.0001**	1.7	0.1518	**9.1**	**<0.0001**	**14.4**	**<0.0001**
coat × tracer × WG	**4.6**	**0.0014**	1.1	0.3632	1.6	0.1893	1.1	0.3347
CON × tracer × WG	**11.7**	**<0.0001**	0.8	0.6542	0.7	0.7966	0.6	0.8568

[a] MC, moisture content (% wb); compression, peak compression force (N); shear, peak shear force (N); TADD20, weight loss after 20 s of grinding in the TADD (tangential abrasive dehulling device). [b] Coat, coating material; CON, conditioning time (h); tracer, type of tracer; WG, theoretical weight gain (%). [c] Results in bold indicate significance level at the 0.01.

easily managing tracer quality consistency in terms of its appearance, weight, dimension, and physical properties. The applied press pressure to compact a formulation varied with the type of tracer due to difference in the flowability and compressibility of the formation. In addition to a compacting force, the tracer production rate was also optimized for each type of tracer. Inappropriate use of a production rate caused overload and jamming in the tablet press and larger variation in tracer quality. A starch-based tracer was manufactured using 100% pregelatinized starch without other additives due to its good flowability and compressibility resulting from starch structural changes caused by gelatinization. With starch polymers, if amorphous regions are dominant, the chains are less ordered and more flexible, resulting in molecular rearrangements during the compression process (*17*). On the contrary, direct compression of SMCC was not sufficient to produce a tracer with appropriate hardness, requiring magnesium stearate for lubrication and a processed sugar for improved binding strength (**Table 1**). When a tracer formulation is compressed, the molecules of a substance are rearranged and become closely packed. This molecular packed structure can increase the crushing strength of tracers (*21*). When higher compacting forces are applied to tracers, increased shearing and compression forces are expected due to a tightly compact structure. Water penetration is more difficult in such a stronger packing structure at swelling (*17*).

Tracer Coating. The surface of the film coating applied to the tracers was found to be smooth with no defects, although there was a characteristic difference among the tracer types and coating solutions. With uniformity of coating mass deposition over the tracer surface, surface roughness can be considered to be an indicator of tracer quality. Improved coating quality can be achieved by strictly optimizing crucial coating process conditions such as coating and drying temperature, tracer surface properties, solubility and viscosity of coating solution, and adequate atomization (*22−24*). Tracer-to-tracer variation in coating is an important factor to be measured to characterize the coating process. Thus, coating variation can serve as a diagnostic tool to identify a defective coating process and assess new processes.

An aqueous film coating system was formulated to prepare a pregelatinized starch coating solution and an HPMC coating solution in which 15% pregelatinized starch with 2% glycerol and 5% HPMC with 1% triethyl citrate were dissolved, respectively (**Table 2**). Starch properties and coating process parameters such as starch source, starch glass transition temperature, starch

dissolution in water, drying temperature, and the moisture content of the samples are known to affect the crystallinity of starch coating films associated with the rheological and mechanical properties of the coated tracers (*25−27*). HPMC coating solution applied under similar coating process conditions for pregelatinized starch produced a coating film without significant defects in the physical appearance of the coated tracer. HPMC is known to be less sensitive than starch to the inlet air temperature on the physical appearance and mechanical properties (*28*). Typically, plasticizers such as glycerol and triethyl citrate are added to the coating formulation to help improve the smoothness, ductility, and flexibility of the coating. The plasticizers used in this study are considered to modify starch and HPMC coatings by weakening the intermolecular attraction between the polymer chains, improving the flexibility and extensibility of the coating film (*29−30*). An increase in plasticizer concentration is expected to decrease the mechanical strength of the coated tracers (*24*).

Overall Characteristics and Properties of Tracers. Each type of tracer required different tablet press settings and a compacting force for the appropriate tracer production. Accordingly, the manufactured tracers were distinctive in weight, dimension, physical, and spectroscopy properties among the types of tracers before and after coating. The results of analysis of variance (ANOVA) (**Table 5**) and mean comparison tests showed that the type of tracer was the most influential factor on moisture content and peak shear force, whereas a conditioning period had the most significant effect on peak compression force in both coated and uncoated tracers.

Uncoated tracers were conditioned at 80% RH and 20.5 °C for 0, 4, 24, and 48 h, which is equivalent to equilibrium relative humidity (ERH) condition for corn at approximately 20% MC wb. Under this condition, sucrose-based tracers absorbed more moisture than the other two types of tracers and disintegrated after a few hours of conditioning. Therefore, they could not be tested for subsequent physical properties without coating. Coated starch-based tracers had a rougher surface than the other two types of tracers and apparent pores and flaws on the exterior of tracers. The surface porosity and the pore structure networks of uncoated and coated tracers are known to be associated with water absorption and penetration and the amount of imbibed marking ink into a unit mass of sample (*31*). The homogeneous matrix of coating likely indicates its good structural integrity (*27*), which improves the mechanical properties of the coated tracers. The pores and cracks of uncoated tracers seemed to influence the

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Table 6. Mean Weight of Sucrose-, Starch-, and Cellulose-Based Tracers before and after Coating[a]

	sucrose-based tracer (g) (CV)[c]		starch-based tracer (g) (CV)		cellulose-based tracer (g) (CV)	
weight gain (%)[b]	pregelatinized starch	HPMC[d]	pregelatinized starch	HPMC	pregelatinized starch	HPMC
uncoated	0.355 (0.79)a[e]		0.288 (1.10)a		0.285 (0.94)a	
1.0	0.359 (0.79)c	0.358 (0.98)b	0.288 (1.16)a	0.289 (0.98)b	0.288 (1.02)b	0.288 (0.58)c
2.0	0.364 (0.64)e	0.362 (0.82)d	0.291 (1.09)c	0.293 (0.99)d	0.291 (0.97)e	0.291 (0.74)de
3.0	0.367 (0.76)f	0.367 (0.88)f	0.293 (0.88)d	0.298 (0.96)e	0.293 (0.80)f	0.294 (0.76)f

[a] Total number of measurements for each type of tracers (n) = 100. [b] Theoretical weight gain (%) of uncoated tracers after coating. [c] CV, coefficient of variation (%). [d] HPMC, hydroxypropylmethylcellulose. [e] Within each type of tracer, data followed by the same letter are not significantly different at $P < 0.01$.

Table 7. Mean and Its Difference in Dimension between Uncoated and Coated Tracers [a]

tracer and coating type	weight gain[b] (%)	thickness (mm) mean	thickness (mm) diff[c]	length (mm) mean	length (mm) diff	width (mm) mean	width (mm) diff
sucrose-based							
uncoated	0	5.141a[e]		11.032a		6.065a	
pregelatinized starch coating	1	5.176a	0.036	11.052b	0.021	6.094b	0.029
	2	5.210bc	0.069	11.074c	0.043	6.118c	0.053
	3	5.230c	0.089	11.096f	0.064	6.146e	0.082
HPMC[d] coating	1	5.178a	0.038	11.084d	0.052	6.122c	0.058
	2	5.201b	0.061	11.091e	0.059	6.131d	0.067
	3	5.237c	0.096	11.130 g	0.099	6.170f	0.105
starch-based							
uncoated	0	4.961a		11.058a		6.146a	
pregelatinized starch coating	1	4.970a	0.008	11.070b	0.012	6.172b	0.027
	2	5.008bc	0.047	11.095c	0.037	6.209c	0.063
	3	5.018d	0.057	11.106d	0.048	6.224d	0.078
HPMC coating	1	5.000b	0.039	11.087c	0.029	6.205c	0.059
	2	5.023c	0.061	11.119e	0.061	6.239e	0.093
	3	5.065d	0.104	11.156f	0.098	6.277f	0.131
cellulose-based							
uncoated	0	4.237a		11.046a		6.077a	
pregelatinized starch coating	1	4.258b	0.021	11.044a	−0.001	6.098b	0.020
	2	4.293c	0.056	11.061b	0.015	6.113c	0.036
	3	4.302c	0.065	11.077c	0.032	6.124d	0.047
HPMC coating	1	4.258b	0.021	11.049a	0.003	6.095b	0.017
	2	4.291c	0.054	11.075c	0.030	6.129d	0.051
	3	4.318d	0.081	11.098d	0.053	6.165e	0.088

[a] Total number of measurements for each type of tracers (n) = 25. [b] Theoretical weight gain (%) of uncoated tracers after coating. [c] Mean difference was calculated by subtracting the mean of uncoated tracer from that of the coated tracer. [d] HPMC, hydroxypropylmethylcellulose. [e] Within each type of tracer for each dimension, data followed by the same letter are not significantly different at $P < 0.01$.

structural integrity and roughness of film coating on the surface because sucrose-based tracers with a smoother and glossier surface showed greater moisture and abrasion resistance of film coatings than starch-based tracers when the same coating material was used. In addition to these factors, tracer manufacturing parameters including compacting force, coating material additives, and coating process conditions also appeared to influence the morphological and mechanical properties of tracers due to the physicochemical and structural changes in tracer polymers induced by the parameter changes. Therefore, tracers with appropriate durability and sustainability during grain shipping and handling would be obtained by controlling and optimizing the manufacturing parameters.

Tracer Weight and Dimension. The tracer weight proportionally increased with a theoretical weight gain (%) after coating (**Table 6**). The increased amount of coating weight was slightly larger in HPMC-coated starch- and cellulose-based tracers than the same tracers with pregelatinized starch coating. However, there was no increase in tracer weight between uncoated starch-based tracer and the pregelatinized starch-coated tracer with 1% weight gain, which may be attributed to poor coating process control and a large variation in uncoated tracer weight. The statistical analysis showed significant interaction between the type of tracer and the coating material on the tracer weight ($P < 0.01$). Apparently, the tracer weight increase by coating varied with the type of tracer and coating material. The tracer weight variation was relatively small. The CV (%) of tracer weight was under or slightly over 1.0% in all uncoated and coated tracers (**Table 6**). As expected from the above observations, starch-based tracer and pregelatinized starch coating showed a larger weight CV (%) than sucrose- and cellulose-based tracers and HPMC coating, respectively. It is speculated that the better flowability and compressibility of the tracer formulation resulted in the smaller weight variation in sucrose- and cellulose-based tracers (*32, 33*).

The uncoated tracer thickness is different between tracers; in order of thickness, sucrose-, starch-, and cellulose-based tracers showed decreasing thickness (**Table 7**). The length and width of sucrose-based tracers, however, were the thinnest, although the same die configuration was used to compress the tracer formulations. This difference in dimension of uncoated tracers can be attributed to the difference in the flowability, compressibility, and compactibility among the formulations. In fact, sucrose-based tracers were compressed at the lower pressure to manufacture the tracer with a hardness similar to that of the other two types of tracers.

After coating, all dimensions of thickness, length, and width increased with a theoretical weight gain. However, the increase of coating film thickness was not the same on each dimension. Apparently, all dimensions of the tracer were not equally exposed to the spray coating. The shape of the cellulose-based tracer appeared to be less feasible for the equal exposure of all dimensions to coating material. In pregelatinized starch coating, there was no difference in length between uncoated cellulose-based tracer and 1% weight gain cellulose-based tracer and a smaller difference between 2% and 3% weight gain coated tracers compared to other types of tracers. This can be attributed to less exposure of the side of the tracer length to coating material during coating process. This nonuniform coating thickness on the tracer surface may be resolved by using a higher coating pan speed (*34*). Increasing pan speed tumbles tracers to create more frequency of exposure to the coating material and improve the coating uniformity. The coating film thickness is also known to be affected by air atomization pressure (*35*).

Similar to tracer weight, variations in the tracer dimensions were small. The CV (%) of the tracer dimensions were < 1% for thickness, length, and width in all coated and uncoated tracers (data not shown). The thickness and width CVs of coated tracers were not significantly different from those of uncoated tracers, indicating that the variations of coated tracers originated more from the uncoated tracers than coating process. HPMC-coated cellulose-based tracers showed the lowest CV (%), which is almost equal to that of uncoated cellulose-based tracer. The variation in coating film thickness is crucial because it can influence mechanical properties and other tracer qualities (*25*).

Statistical analysis showed that type of tracer, coating material, weight gain, and their interactions had a significant effect on the final tracer dimension. The tracer dimension significantly differed with the type of coating material ($P < 0.01$). The HPMC coating solution produced a tracer with a thicker film coating. An increase of coating thickness caused by coating application depended on the type of tracer ($P < 0.01$). The three types of tracers with the same theoretical weight gain exhibited a different coating thickness in the application of the same coating material. This might be due to the difference in the exterior and interior structural property between uncoated tracers (*36*). These results seem to demonstrate that the combination of the type of tracer and coating material needs to be optimized to produce tracers of better quality and performance.

Moisture Absorption of Tracers. After conditioning at 80% RH and 20.5 °C for 0, 4, 24, and 48 h, the moisture content (MC) of tracers increased and was almost double the initial content at 48 h (**Figure 2**). Uncoated starch-based tracers appeared to absorb more moisture than cellulose-based tracers. Starch-based tracers revealed moisture absorption behavior similar to that of wheat or maize, whereas cellulose-based tracers did not absorb much water after 24 h of conditioning. Starch-based tracers are hygroscopic and contain abundant hydroxyl groups of amylose and amylopectin chains for fast hydration. The absorbed water is thought to serve as a plasticizer in starch-based tracers, changing the rheological and mechanical properties of tracers (*22, 37*). Dissolution of uncoated sucrose-based tracers is attributed to the hydration of hydroxyl group of sucrose molecules. Conversely, the cellulose molecule has a low tendency to absorb moisture. The true and bulk density of the matrix is an important factor that is inversely correlated with porosity and water penetration (*38−41*). In this study, cellulose-based tracers exhibited a higher density (1.545 g/cm³) than the starch-based tracers (1.487 g/cm³). With a lower hygroscopic property, the higher density and more compact structure of cellulose-based tracers might result in less moisture uptake. The higher equilibrium water content of starch-based
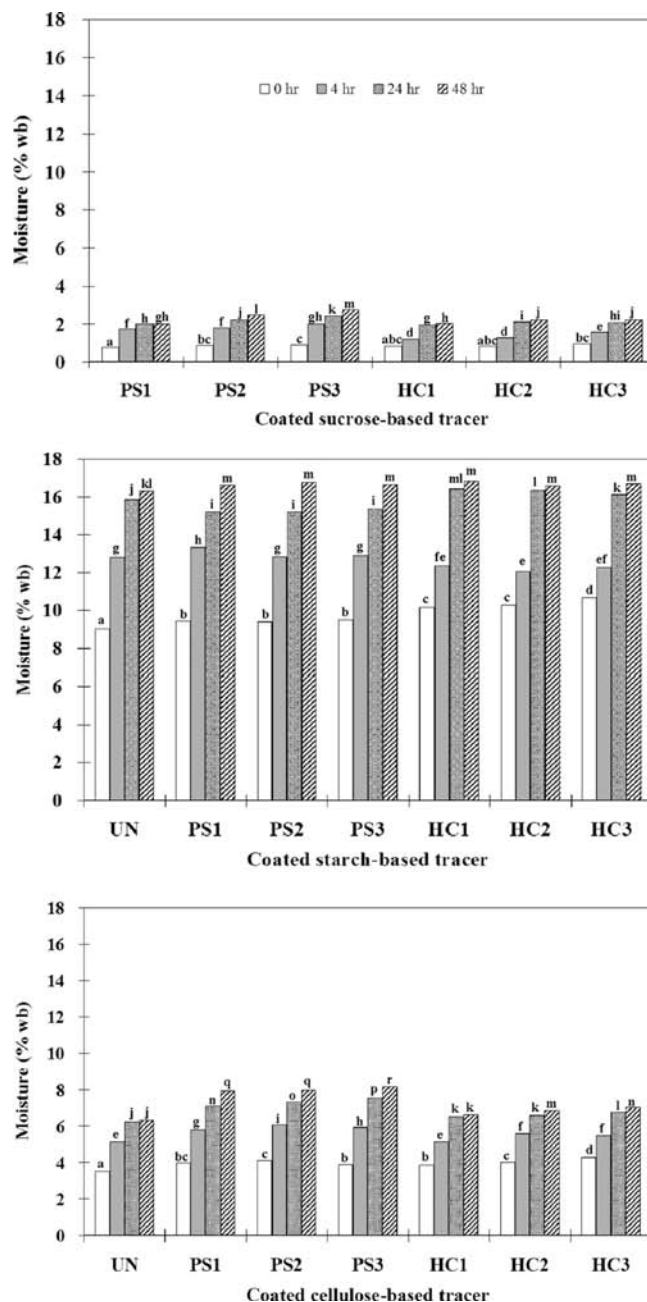

Figure 2. Moisture content (% wb) of tracers with different weight gains under conditioning at 80% RH and 20.5 °C for 0, 4, 24, and 48 h. UN, PS, and HC represent uncoated tracer, pregelatinized starch coating, and HPMC coating, respectively. Numbers following PS and HC indicate the percent of weight gain by coating application. Uncoated sucrose-based tracers were not tested due to the dissolution during conditioning. Within each type of tracer, data followed by the same letter are not significantly different at $P < 0.05$.

tracers is also considered to be associated with a more porous structure of the tracer surface (mainly fine pores) and internal texture (larger pores) (*34, 42*).

The ANOVA test results showed that the moisture content of coated tracers was significantly influenced by the type of tracer, coating material, conditioning period, and theoretical weight gain ($P < 0.01$) (**Table 5**). The increase of moisture content in HPMC-coated tracers was a little lower than that of uncoated tracers conditioned for 4 h in starch-based and cellulose-based tracers. The moisture content increased in proportion to a theoretical weight gain in coated sucrose- and cellulose-based tracers during

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conditioning. However, starch-based tracers did not show a significant moisture increase accompanied by a weight gain, presumably due to being close to the maximum water absorption capacity in the early conditioning period. The use of pregelatinized starch in the tracer formulation and coating material may be considered as a factor to contribute to the higher moisture uptake in starch-based tracers and pregelatinized starch-coated tracers because starch gelatinization can lead a molecular reorganization to increase water absorption capacity (*27*).

As for coating material, sucrose- and cellulose-based tracers coated by HPMC showed lower moisture contents than the same types of tracers coated with pregelatinized starch. However, starch-based tracers showed an opposite tendency, that is, slightly higher moisture content for HPMC-coated tracers. This demonstrates that the final moisture content of coated starch-based tracers was mainly determined by higher hygroscopic pregelatinized starch ingredient in a tracer rather than HPMC film coating. In all three types of coated tracers, the increase of moisture content from 24 to 48 h of conditioning was higher in pregelatinized starch coating than HPMC coating. It is known that the pregelatinized starch film is relatively more sensitive to humidity and becomes unstable in a high-moisture environment (*27*). In addition to pregelatinized starch in a coating formulation, the hygroscopic character of the plasticizer added to the formulation may increase that of pregelatinized coating films. The plasticizer is related to the structural modification of the polymer network to make the coating film favor water adsorption and prevent fracture of the film during handling and storage (*27*). As a result, the concentration of plasticizer can affect the mechanical and rheological properties of the coating film (*22, 37*).

Peak Shear Force of Tracers. Sucrose-based tracers exhibited lower shear strength (about half) than other types of tracers regardless of the presence or absence of a coating material throughout the conditioning period (**Figure 3**). The lower shear strength of sucrose-based tracers with the highest density was rather unexpected. This may be explained by a relatively higher concentration of lubricant (magnesium stearate) and lower compacting force used for manufacturing sucrose-based tracers. The particles in such a less closely packed tracer structure might be bound less tightly by the physicochemical binding forces, consequently decreasing the shear and compressive strengths of the tracer (*21*). There was no significant difference in the shear strength of a coated tracer between 24 and 48 h of conditioning. The shear strength decreased more in cellulose-based tracers as the conditioning period progressed. Unlike other types of tracers, uncoated and 1 and 2% weight gain starch-based tracers coated with pregelatinized starch showed increased shear strength at 4 h of conditioning, particularly in uncoated tracers. The hydration of pregelatinized starch and water's action as a plasticizer could lead starch molecules to a more ordered structure (*21, 22, 37*), increasing the mechanical strength of the tracer, up to a certain moisture content. The increase of moisture uptake beyond 24 h was not accompanied by a drop in the shear strength of starch-based tracers. In general, the shear force of coated tracers was improved by increasing the amount of coating application. Increasing coating material and coating thickness are expected to produce tracers having greater shear strength (*43*). The improvement of shear strength was more pronounced in HPMC-coated tracers than in pregelatinized starch-coated tracers, which may be accounted for by the more homogeneous matrix and the larger amount of HPMC coating disposed on the tracer surface (*27*).

Peak Compression Force of Tracers. Both uncoated starch- and cellulose-based tracers had a significant drop in compressive strength after 4 h of conditioning. Both became easily broken
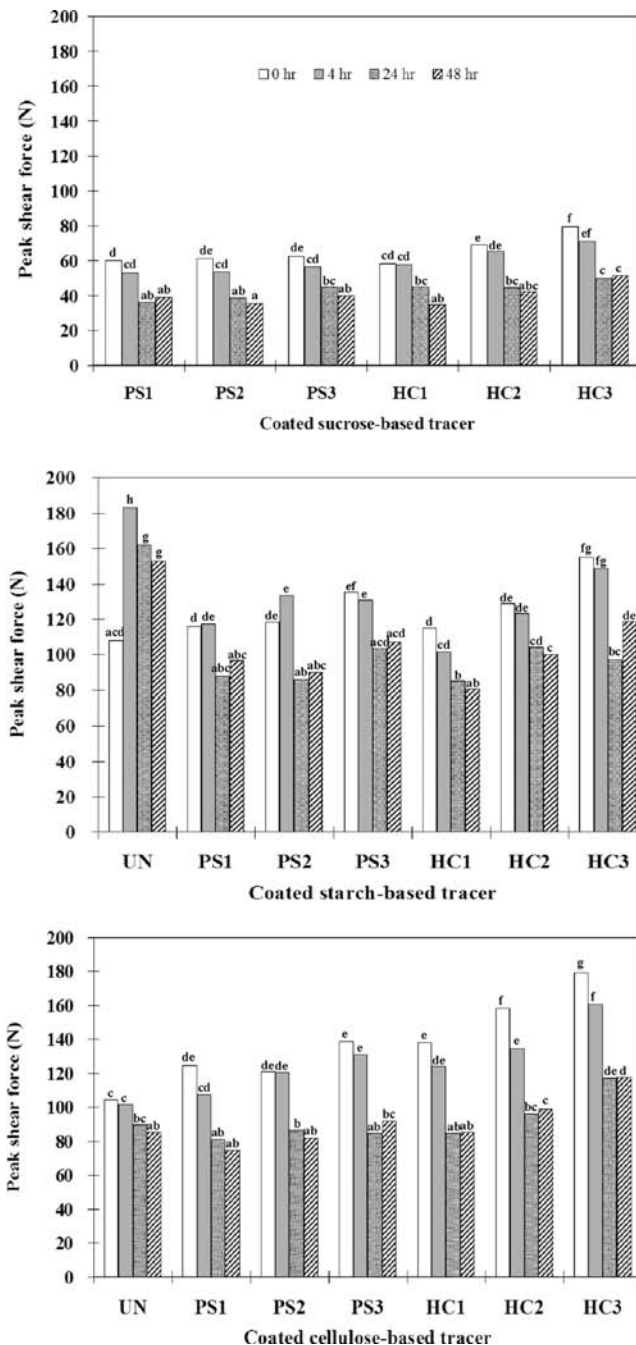

Figure 3. Peak shear force (N) of tracers with different weight gains under conditioning at 80% RH and 20.5 °C for 0, 4, 24, and 48 h. UN, PS, and HC represent uncoated tracers, pregelatinized starch coating, and HPMC coating, respectively. Numbers following PS and HC indicate the percent of weight gain by coating application. Uncoated sucrose-based tracers were not tested due to the dissolution during conditioning. Within each type of tracer, data followed by the same letter are not significantly different at *P* < 0.05.

by low pressure at and beyond the 8 h of conditioning. However, sucrose-based tracers were less influenced and even displayed an increase in compressive strength in HPMC-coated tracers at 4 h of conditioning. Apparently, the coating application improved the compressive strength of uncoated tracers, particularly cellulose-based tracers coated with HPMC (**Figure 4**). Overall, HPMC-coated tracers revealed a greater compressive strength than pregelatinized starch-coated tracers throughout the conditioning period. In ANOVA test results, the conditioning period and type
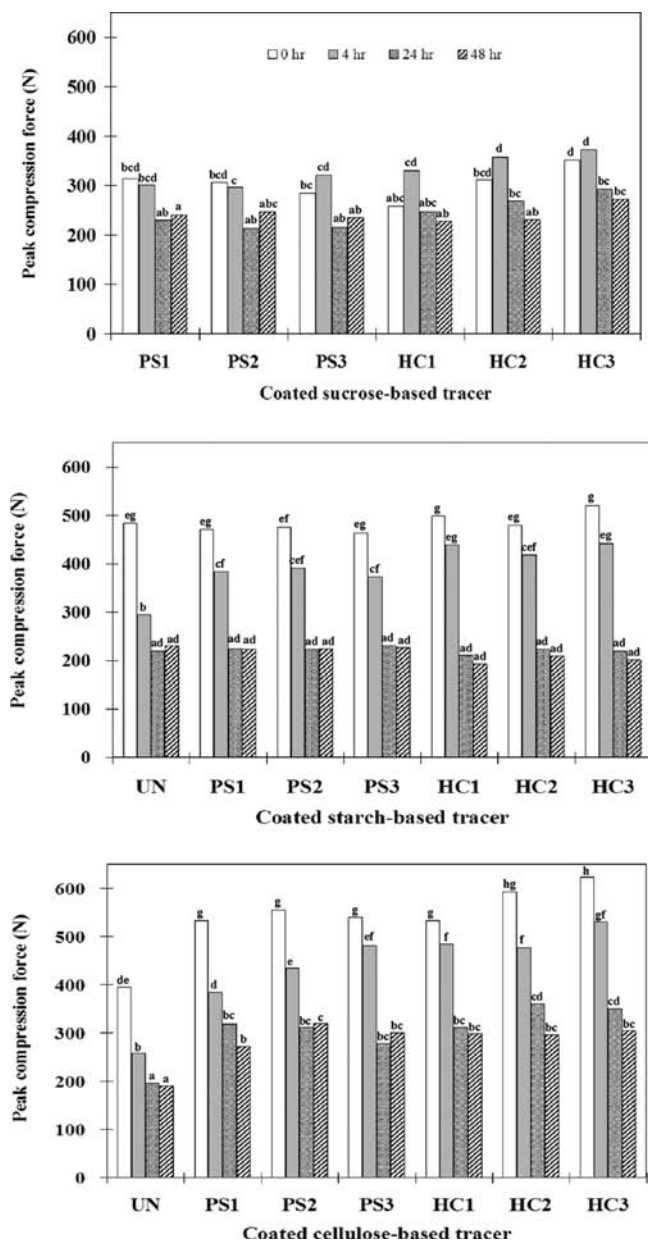
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Figure 4. Peak compression force (N) of tracers with different weight gains under conditioning at 80% RH and 20.5 °C for 0, 4, 24, and 48 h. UN, PS, and HC represent uncoated tracers, pregelatinized starch coating, and HPMC coating, respectively. Numbers following PS and HC indicate the percent of weight gain by coating application. Uncoated sucrose-based tracers were not tested due to the dissolution during conditioning. Within each type of tracer, data followed by the same letter are not significantly different at $P < 0.05$.

of tracer were more significant factors on the peak compression force of coated tracers, whereas the compressive strength did not increase proportionally as weight gain and coating film thickness increased (**Table 5**). Prior to conditioning, the compression strength of HPMC-coated tracers was positively correlated with weight gain. However, starch- and cellulose-based tracers coated with pregelatinized starch did not exhibit the greatest compression force at 3% weight gain. This nonproportional increase of compression strength with weight gain and film thickness in pregelatinized starch coating might be attributed to an increase in flaw or weakness of film coating with a weight gain (*25*). Fundamentally, the compressive strength of tracers should withstand pressures during grain storage and handling. The tracers

tested in this study appeared to be strong enough using Janssen's equation (*44*) to estimate pressures at the bottom of storage bins of various dimensions.

Tangential Abrasive Dehulling Device (TADD) Test of Tracers. Unlike any other physical property, the ANOVA results showed that coating material was the most influential factor followed by the type of tracer on weight loss during grinding ($P < 0.01$) (**Table 5**). In general, HPMC-coated tracers had less weight loss than pregelatinized starch-coated tracers, depending on the type of tracer and the conditioning period. The nonplasticized HPMC coating film has rheological and mechanical properties similar to those of the nonplasticized starch coating film, whereas the plasticized HPMC coating film is more flexible and less brittle, which may help protect the tracer against mechanical damage and weight loss during grinding (*22*). Weight loss of tracers by grinding increased with grinding time within the range of $0-20$ s regardless of coating application (**Figure 5**). Starch-based tracers were more susceptible to weight loss than other types of tracers by grinding. Sucrose-based tracers had a similar weight loss in both coating materials, which was more pronounced after 20 s of grinding, implying that the lesser weight loss of sucrose-based tracers was more associated with the tracer itself rather than the type of coating material. The conditioning period, the major influential factor on the other physical properties of tracers, significantly affected weight loss at 20 s of grinding ($P = 0.0135$). Zero hour conditioning produced the least amount of weight loss in uncoated tracers, but not in coated tracers. A weight loss of HPMC-coated tracers generally increased with conditioning period. Contrarily, an inconsistent weight loss with conditioning period was observed in pregelatinized starch-coated tracers. This might be explained by the fact that starch coating materials are sensitive to humidity and become unstable (*27, 45*). An increase of coating weight gain led to less weight loss of HPMC-coated tracers, whereas a coating weight gain appeared to be uncorrelated to weight loss in pregelatinized starch-coated tracers.

Data Analysis and Multivariate Statistical Analysis of Raman Spectra. The baseline-corrected and normalized Raman spectra of ingredient powders and manufactured tracers are presented in **Figure 6**. The spectral difference between the powders and tracers was noticeable. The major difference in all three types of tracers was in the wavelength range from 2800 to 3150 cm^{-1} correlated with C−H stretching mode (*46*). In **Figure 6**, the Raman signal of uncoated sucrose-based tracer appeared similar to that of processed sugar powder consisting of 97% of the tracer. New bands were observed in the tracer spectrum at 1062, 1295, and 2845 cm^{-1} associated with magnesium stearate. The processed sugar and sucrose-based tracer showed the higher Raman band intensity at 401 and 848 cm^{-1} corresponding to C−O or C−C vibrations of sucrose (*47*). The subtraction of bands associated with magnesium stearate from uncoated sucrose-based tracer spectrum gave a spectrum close to that of processed sugar. The slight difference between the subtracted and the spectrum of the processed sugar may be partially explained by the temperature increase on tracer compaction, which may induce structural changes in the ingredient depending on its glass transition temperature and storage time, consequently influencing mechanical properties and Raman band intensity (*48, 49*). The main spectral regions for interpretation and characterization in Raman spectrum of pregelatinized starch powder and uncoated starch-based tracer were located below 1500 cm^{-1} and above 2800 cm^{-1} (**Figure 6**). Both powder and tracer showed strong Raman band intensities at 480 cm^{-1} due to a C−O vibration and at 940 cm^{-1} corresponding to vibrations originating from the α-1,4 glycosidic linkages in starch (*46*). The pyranose ring of glucose unit in starch

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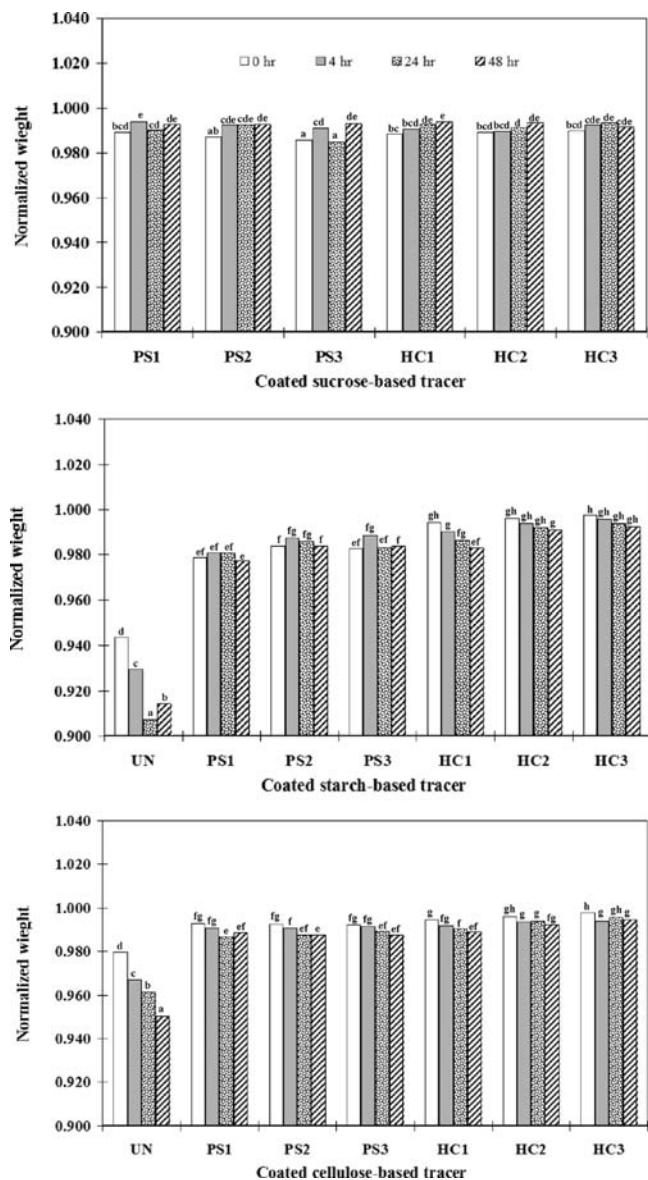*J. Agric. Food Chem.,* Vol. 58, No. 20, 2010   **10953**

Figure 5. Normalized weight of tracers with different weight gains during 20 s of TADD grinding under conditioning at 80% RH and 20.5 °C for 0, 4, 24, and 48 h. UN, PS, and HC represent uncoated tracers, pregelatinized starch coating, and HPMC coating, respectively. Numbers following PS and HC indicate the percent of weight gain by coating application. Uncoated sucrose-based tracers were not tested due to the dissolution during conditioning. Within each type of tracer, data followed by the same letter are not significantly different at *P* < 0.05.

may be identified and characterized with bands at 440, 480, and 576 cm^{-1} in both pregelatinized starch power and tracer (*46*). Any Raman bands in the range from 1630 to 1657 cm^{-1} due to amylose and amylopectin were not noticeable, implying changes in amylose and amylopectin environments due to chemical modification of starch. The Raman band at 862 cm^{-1} due to CH and CH$_2$ deformation for pregelatinized starch appeared to be shifted to 860 cm^{-1} for uncoated tracer. This may be attributed to structural change of starch granules due to temperature increase during pregelatinized starch powder compaction (*49, 50*). A large difference in the wavelength range from 3000 to 3500 cm^{-1} corresponding to the O−H stretching of water molecules may suggest changes in the arrangement and distribution of water molecules in a compact structure of starch-based tracer (*46*). The biochemical and structural properties of cellulosic

materials have been studied by Raman spectroscopy in different areas (*47, 51−53*). Because cellulose-based tracer was made from a mixture of SMCC and processed sugar, the tracer spectra showed intense bands from the two tracer ingredients. Several strong bands in the tracer spectrum from the processed sugar include bands at 400, 553, 918, 1014, 1040, 2911, 2942, 2986, and 3015 cm^{-1}. Apparently, there was no interference from processed sugar in the Raman spectrum of SMCC, which could be confirmed by comparing the raw spectra of tracer with the combined spectra of two ingredients. The band intensities at 457 and 607 cm^{-1} of SMCC become weaker in the tracer spectrum, and the band at 457 cm^{-1} apparently shifted to 434 cm^{-1}. This also occurred at the prominent cellulose Raman band at 1095 cm^{-1}. This band was shifted to lower wavelength and overlapped with the 1087 cm^{-1} band of processed sugar to form a broader band.

The difference between coated tracer spectrum and uncoated tracer spectrum was observed in all tracer and coating types (**Figure 6**). The extent of the difference was dependent on the amount of coating materials deposited on tracers. The Raman band intensity decreased as theoretical coating weight gain increased. This may be explained by attenuation of uncoated tracer Raman spectrum due to coating materials (*54, 55*). Differences in Raman band intensities of coated tracers were not identical between 1 and 2% and between 2 and 3% theoretical weight gains in HPMC-coated sucrose- and starch-based tracers. This may be due to inhomogeneous surface coating at the spectral sampling areas of selected samples as well as the irregular baseline contributing to the spectra (*55*). In general, tracers with 3% theoretical weight gain exhibited a lower spectral variation than those with 1 and 2% theoretical weight gains, which may be attributed to the more uniform production of Raman spectral features of tracers with the higher theoretical weight gain (*56*).

Raman spectroscopy in combination with appropriate data treatment can extract relevant and essential spectral information for quality and quantity measurements of coating and tracer ingredients even under fluorescent conditions (*54−57*). There are different approaches and algorithms for spectral data processing aiming to minimize the effect of instrument and decompose the spectral profile to improve the spectral resolution. In the present work, the Savitzky−Golay derivative smoothing techniques (*58*), which use several original data points in the spectrum to calculate the derivatives to maximize spectral differences, were applied for further improvement of the models developed with the baseline-corrected and normalized spectral data. The spectra transformed into their derivatives were used as the input for performing PCA and cluster analysis to investigate model efficiency in differentiating tracers according to their types and coating levels.

Multivariate statistical techniques can provide multidimensional vectors to carry more spectral information than single wavelengths, resulting in more integrated and robust models for identifying and classifying the tracer and coating types and coating thickness (*59*). By PCA of Raman spectra, more than 400 wavelength variables were reduced to only about 25 latent variables (principal components). The wavelengths with the larger loading in PCA have the higher relevance for cluster formation (*47*). **Figure 7** presents the two-dimensional scatter plots of principal component scores for each type of tracer, which visualizes the spectral differences between coating types and between coating weight gains according to the scores. As an example, in sucrose-based tracers, the first principal component score discriminates tracers by coating thickness, whereas the second principal component score differentiates coating types. The PCA results can be used to construct a model to measure the variability in tracer quality and ingredient powder by evaluating the deviations using the model (*55*).
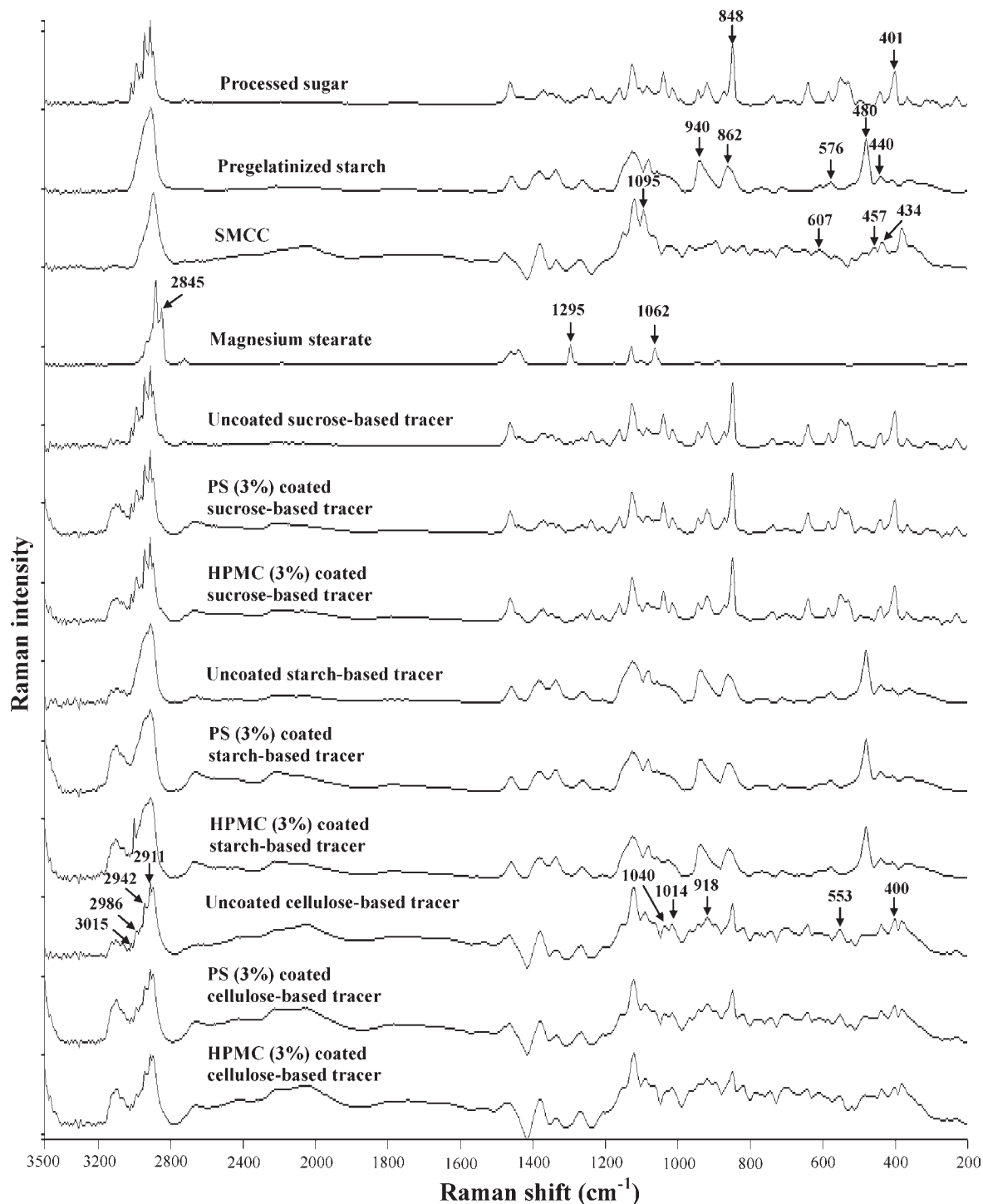
Figure 6. Raman spectra of ingredient powders and manufactured tracers. SMCC, PS, and HPMC represent silicified microcrystalline cellulose, pregelatinized starch, and hydroxypropylmethylcellulose, respectively.

Cluster analysis performed using the first and second derivatives of Raman spectra in the whole range allowed classification of tracers into a few exclusive groups with similar spectral properties. As expected, the classification was configured on the basis of coating types and coating weight gains, although starch- and cellulose-based tracers were not well separated (**Figure 7**). The first and second derivatives offered significant improvement in accuracy of classifying tracers compared to the baseline-corrected and normalized spectra. However, there was no difference in classification performance and outcome between two derivatives for sucrose- and cellulose-based tracers, whereas starch-based tracers might have a little more advantage from

the first-derivative computation in classification (**Figure 7**). These results reemphasize the importance of selecting appropriate data pretreatment procedure and algorithms for improving the spectra and reducing matrix interference. The classification results from the hierarchical Ward's minimum variance method (*60*) that determines clusters by minimizing a sum of squares within each cluster showed clear discrimination between uncoated and coated tracers in all three tracer types and moderate separation between coating types. However, except for sucrose-based tracers, limited success and poor classification results were obtained for differentiating starch and cellulose-based tracers by theoretical coating weight gain. This might be attributed to a less homogeneous and
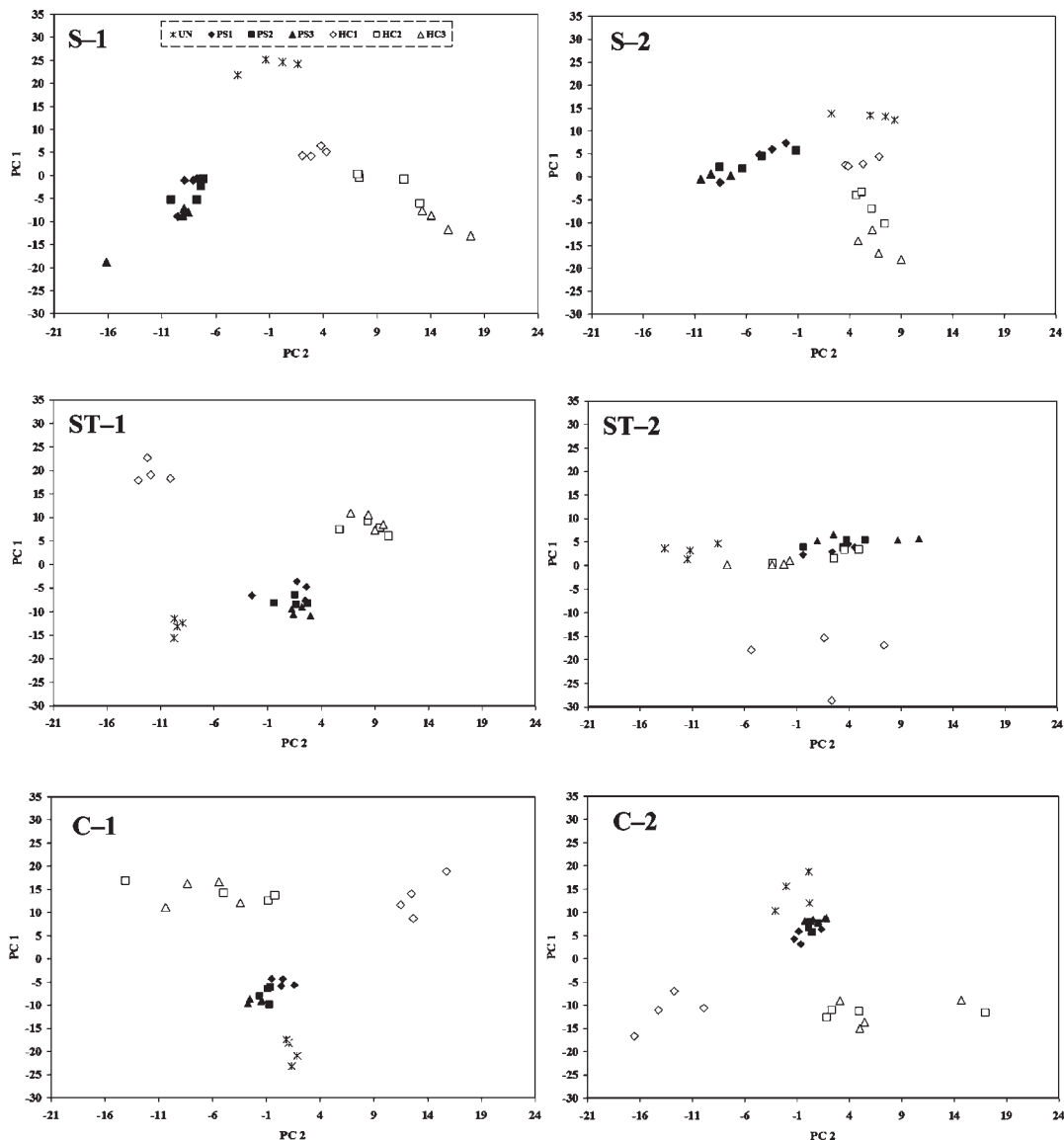
Figure 7. Scatter plots of the first two principal component (PC) scores through the principal component analysis of the Savitsky−Golay first (1) and second (2) derivate spectral data. S, ST, and C stand for sucrose-, starch-, and cellulose-based tracers, respectively. UN, PS, and HC represent uncoated tracers, pregelatinized starch coating, and HPMC coating, respectively. Numbers following PS and HC indicate the percent of weight gain by coating application.

rougher coating surface and nonrepresentative sampling in the two types of tracers (*55,61*). Apparently, pregelatinized starch-coated tracers were less distinctively separated by a theoretical coating weight gain than HPMC-coated tracers. This may be partially explained by thicker HPMC coating. The thicker coating typically gives more homogeneous and consistent Raman spectra (*56*).

As demonstrated in the present work, Raman spectroscopy, requiring less analysis time and little sample preparation, is an attractive and promising technique for the proposed grain traceability system because it can provide rapid quality and process control of tracer and coating. In addition, this technique can serve as a fast and reliable tool for distinguishing genuine tracers from counterfeit tracers dispensed into bulk grains by terrorist or organized criminal groups.

In conclusion, three types of tracers, sucrose-, starch-, and cellulose-based tracers made of and coated with food-grade substances, had acceptable durability and strength characteristics suitable for handling and storing with grain presumably without any significant changes in their quality and performance. The results from this study draw attention to a need to carefully

formulate a tracer mixture and coating solution and design the tracer manufacturing processes to yield tracers with desirable properties and characteristics.

To maintain consistent quality and superior performance of a tracer resistant to damage from moisture and mold growth, the tracer formulation would be required to have a low hygroscopic property and excellent flowability, compressibility, binding strength, and compactability. With respect to coating, the coating material also needs to be less hygroscopic, flowable, and ductile to provide a smooth and homogeneous matrix of coating film on the surface to enhance tracer strength and protecting a printed ID code from mechanical damage. It is equally important to select tracers with fewer surface defects and optimize coating process conditions to achieve the uniformity and consistency of tracer coating. In addition, variation in tracer manufacture and coating processes should be minimized because it appeared to influence the mechanical, structural, and spectroscopic properties of a coated tracer, making it difficult to explain the quality factors of a tracer governing its performance.

The U.S. Food and Drug Administration expressed no objection to insertion of a food-grade tracer in grain without

adulterating the grain. Future research to develop new tracers would investigate alternative sizes and shapes of tracers for new crops, modify current tracer and coating formulations with novel substances possessing the aforementioned physicochemical properties, and establish new manufacturing process conditions. The characteristics of newly designed tracers should be as follows: (1) more durable and better for flowing with grains during handling and storage; (2) more resistant to moisture and mechanical damages; (3) economically cheaper to manufacture; (4) easier to manage and keep clean, and (5) more flawless and ink-absorbent surface for printing ID codes.

ABBREVIATIONS USED

ANOVA, analysis of variance; CV, coefficient of variation; HPMC, hydroxypropylmethylcellulose; PCA, principal component analysis; MC, moisture content; MCC, microcrystalline cellulose; SMCC, silicified microcrystalline cellulose; TADD, tangential abrasive dehulling device.

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