Production of Amorphous Starch Powders by Solution Spray Drying

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ABSTRACT: The spray drying of starch/maltodextrin formulations was evaluated as a potential technology for the manufacturing of amorphous thermoplastic starches. Mixtures of starches with high to low amylose (Am)–amylopectin (Ap) ratios were spray-dried from water-based solutions and granular dispersions. The effects of the feed composition on the morphology and physical properties of the end product were investigated with the spray-drying conditions kept constant. Powders obtained from the starch solutions were totally amorphous, and the particle size characteristics were not affected by the applied variations in composition. The particles obtained from the solution-dried formulations were small, highly irregular, and shriveled, and the bulk densities were low. Independent of the Am/Ap ratio, the particles could easily be redissolved and showed low viscosities. The spray-dried powders obtained from the starch–water dispersions very much retained the granular structure present in the native components. All showed viscosities, crystallinity patterns, gelatinization, and powder flow characteristics in line with expectations for Am/Ap-based granular mixtures. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: amorphous; biomaterials; morphology

INTRODUCTION

The development of flexible packaging materials based on biodegradable materials has recently attracted a lot of research.[1] Within the classes of synthetic and natural materials tested, starch has become a popular choice, as it is readily available from different renewable resources and can be obtained in a range of different blend ratios of its main constituents: amylose (Am) and amylopectin (Ap).[2] For the manufacturing of films and sheets, starch is plasticized with water in combination with low-molecular-weight chemicals that interact with the starch backbones through hydrogen bonding. Familiar examples are urea, glycol, glycerol, threitol, xylitol, glucose, and maltose.[3,4] The processing of these so-called thermoplastic starches (TPSs) in general is performed through a combination of low to high shear dry mixing in tumblers or planetary mixers[5] followed by calendaring, sheet extrusion, or pellet compression.[6] Alternatively, the components can be directly mixed and extruded.

A major drawback of using TPS to manufacture packaging and coating materials is the slow recrystallization of starches (retrogradation), which results in the loss of mechanical properties, such as brittleness and tensile properties.[7] Several studies have focused on the interaction between plasticizers and starch,[4,7] the mutual interaction between plasticizers,[5] and the identification of means to reduce or delay retrogradation.[8] In general, these TPS systems are manufactured in the presence of water–plasticizer combinations, which either are dried to study the plasticizer–starch interaction or are studied as amorphous water–plasticizer–starch blends to evaluate retrogradation in wet environments.

Combinations of plasticizers and water lead to retrogradation through the recombination of Am and Ap, and for some plasticizers (maltodextrin), it has been reported that water is expelled during the process[6] and crystallization is promoted. To overcome this disturbing influence of water but maintain the plasticizer activity during the manufacturing process, another thermal processing route may be needed to obtain dry amorphous starch–plasticizer blends.

For this reason, the spray drying of TPS blends from starch–water dispersions and solutions has been investigated. The spray-drying processes, as applied to native starch solutions, has remained underdeveloped, although this technology is considered an important way to produce amorphous materials[9] or, in particular for native starches, to manufacture small particles.[10] In this article, we report the initial part of a study in which different Am/Ap blends were spray-dried for the purpose of the

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TABLE I
Ratios and Codes Used for Sample Preparation

	Am (%)	Ap (%)	Code	Code description
Native (as received)	70	30	Am-N	Native amylose
Solution	70	30	Am-S	Solution-dried amylose
Solution	53	47	Am–Ap-S	Solution-dried amylose–amylopectin
Solution	27	73	Ap-S	Solution-dried amylopectin
Native (as received)	27	73	Ap-N	Native amylopectin
Dispersion	70	30	Am-D	Dispersion-dried amylose
Dispersion	53	47	Am–Ap-D	Dispersion-dried amylose–amylopectin
Dispersion	27	73	Ap-D	Dispersion-dried amylopectin

All samples contained 33 wt % maltodextrin (DE-16) on a solid basis.

subsequent processing of these materials into TPS films. Gelatinized starch solutions were made in an autoclave reactor; then, both dispersions and solutions were spray-dried. The obtained starch powders were characterized before and after the drying process. In particular, the effect of solution spray drying on the powder properties was studied for Am–Ap–maltodextrin blends. The morphology, crystallinity, particle size distribution (PSD), level of gelatinization, viscosity, thermal properties, and flow properties of the powder granules were systematically studied and analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), laser diffraction, isobaric and isothermal treatments, conventional differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC), and bulk density/tap density measurements.

EXPERIMENTAL

Materials

The materials used in this study consisted of high native amylose (Am-N) cornstarch with a 70% Am content, waxy cornstarch with a 27% Am content, and a binding agent maltodextrin (DE-16), used to accommodate the spray drying of the TPS solution to control dryer fouling and minimize the stickiness of the product,[3,11] although maltodextrin was reported to stimulate the retrogradation of starch.[6] All of the starting materials were obtained from Sigma-Aldrich. The coding of the samples used in this study is given in Table I.

Sample preparation

High-Am-N and waxy cornstarch were dispersed in distilled water (3% w/v) at room temperature. The dispersions were prepared by magnetic stirring at ambient pressure and temperature. The dispersions were continually stirred to keep them well mixed and to prevent gel formation. Then, 1 g (33% w/w of starch) of a binding agent was mixed into the dispersion. The preparation of a homogeneous TPS so-lution in water requires elevated temperatures. An autoclave reactor was used to dissolve the starch at 140°C and 10 bar of nitrogen pressure with stirring at 600 rpm (3% w/v in water). High-Am-N and waxy cornstarch were mixed in different ratios, as described in Table I.

Spray drying

The starch solutions and dispersions were fed into a Buchi (B-191, CH-9230 Flawil, Switzerland) mini spray dryer for drying. The spray dryer functioned according to the parallel flow (cocurrent) principle. To achieve optimal atomization performance in the dryer, a supply of compressed air with a pressure of 5–8 bars was necessary. Constant equipment settings and drying conditions were used for spray drying. The operating conditions were as follows: aspirator rate = 100%, drying air temperature (inlet temperature) = 130°C, a pump rate dependent on the outlet temperature and feed concentration, air pressure = 5 bar, flow rate = 600 L/h, and a nozzle cleaner set to 1 (60 strokes/min). The system was kept running after the completion of the experiment, with the heating element turned off until the air outlet temperature fell below 70°C. The samples were then collected for measurements and characterization.

Powder analysis

To evaluate the effects of spray drying on both solutions and dispersions containing different Am/Ap ratios, the properties of the obtained TPS powders were investigated with the help of different analytical techniques.

Moisture content

The moisture contents of the TPS powder granules were analyzed immediately after sample preparation with the weight loss method. All of the samples (8 g each) were dried for 4 h at 105°C.[12] The weight of each sample was then measured, and the differences

in weight were taken to calculate the moisture contents (percentages).

Particle morphology

SEM was performed with a JEOL 6320 F scanning electron microscope Jeol LTD. Tokyo, Japan. Before analysis, the samples were covered with a thin palladium/platinum conductive layer created with a Cressington 208 sputter coater (Elektronen-optik-service GmbH, D44319 Dortmund, Germany).[13] Scanning electron micrographs were taken to observe and investigate the surface morphology and shape structure.

Crystalline structure

The crystalline structures of the spray-dried samples were studied with an X-ray diffractometer (Bruker D8, D76181 Karlsruhe, Germany). The XRD system was operated at 40 kV and 40 mA, and diffractograms of the granules were recorded from a 2θ value of 5° to a 2θ value of 40° with a scanning speed of 1 s and a step size of 0.02°. Copper was used as the XRD element with a wavelength of 1.54 Å.

PSD

The volume PSD of the spray-dried TPS powders were determined with a laser diffraction technique [Helos particle size (PS) analysis, Helos H1988 (System-Partikel-Technik, D-38678 Clausthal-Zellerfeld, Germany) and Rodos R3 (System-Partikel-Technik, D-38678 Clausthal-Zellerfeld, Germany): 0.5/0.9 to 175 μm]. A powder dispersing pressure of 3 bars was selected and used for the PSD determination of all of the samples. All of the measurements were done in triplicate. The average PSD for all samples was calculated by software provided by (System-Partikel-Technik, D-38678 Clausthal-Zellerfeld, Germany).

Powder flow properties

The powder flow characteristics were evaluated by various methods. These methods included the measurement of the bulk density, tap density,[14] Carr's compressibility index (CI),[15] and Hausner ratio (HR).[16]

Bulk density

The bulk densities of the samples were measured by the weight and volume procedure. We determined the bulk density of the samples by weighing 20 g of powder sample into a 100-mL graduated cylinder. The cylinder with sample was knocked gently five times on the rubber mat to make the surface of the sample smooth for reading the volume. The volume was noted, and the results are presented in grams per milliliter.[12]

Tap density

The tap densities of the samples were measured with a Vankel tap density tester (model STAV 2003, JEF, Germany). A TPS powder sample (30 g) was placed in a graduated cylinder, and the initial volume of the sample in the cylinder was measured. The weight of the TPS powder sample was recorded, and then, the sample was mechanically tapped with the Vankel tap density tester. The cylinder was tapped 750 times, and the tapped volume of the powder was measured to the nearest graduated unit. The tap density was calculated by division of the mass of the sample by its final tapped volume.

Carr's CI and HR

The bulk and tap densities were used to calculate Carr's CI [eq. (1)] and the HR [eq. (2)] as indicators for the flow properties and compressibility of the powders[17]:

$$CI = \frac{\rho_{tap} - \rho_{bulk}}{\rho_{tap}} \times 100 \qquad (1)$$

$$HR = \frac{\rho_{tap}}{\rho_{bulk}} \qquad (2)$$

where ρ_{tap} is the tap density and ρ_{bulk} is the bulk density.

Isothermal and isobaric treatments

Isothermal and isobaric treatments were used to understand the effects of the temperature and pressure on the phase transition of 5% (w/v in distilled water) maize starch dispersions and solution-dried TPS powders with different Am and Ap contents, as described previously.[18,19] Buckow and coworkers[18,19] used a temperature range of 50–110°C for isothermal treatment and 6500 bar for isobaric treatment at 30°C.

In this study, a slightly modified procedure was used for both the solution- and dispersion-dried samples. Isothermal treatments of different samples were done at 60°C and ambient pressure. Treatment was carried out in sampler vials (4 mL) in a temperature-controlled oil bath, with 1.5-mL starch samples used for the isothermal treatment. After the target temperature, that is, 60°C, was reached, the samples were kept for 5 min at that temperature. The samples were then immediately withdrawn and cooled in ice water for 60 min. The samples were analyzed by detection of the loss of optical birefringence under a (Zeiss MRO 55 Axioskop, West Germany) microscope equipped with a polarization filter. The same procedure was repeated three times to investigate the loss of birefringence and to observe the degree of gelatinization.

The ice-cooled samples (from the isothermal test) were then placed in a pressure vessel. Isobaric treatment of the starch dispersions was carried out in an autoclave reactor at 75°C and 50 bars. When the reactor reached the target temperature, decompression was started. A thermocouple was inserted directly into the sample vials to measure the temperature of the samples. The decompression rate was standardized at 8 bar/min. After pressure release, the samples were immediately removed from the reactor vessel and stored on ice for at least 15 min. The samples were again analyzed under the microscope to detect the loss of optical birefringence.

Viscosity

Viscosity measurements were carried as described previously with some modifications.[20] The solution- and dispersion-dried samples were prepared for viscosity measurement as follows: 100-g quantities of starch slurry (5% solids) were heated at 120°C for 7 min in a stirring (400-rpm) autoclave reactor under 5 bars of pressure. The reactor was heated to 120°C and kept there for 3 min, and then, the sample was taken directly from the reactor. The final viscosity was measured with a Brookfield (DV II, Middleboro, MA 02346, USA) at 50°C and 100 rpm.

Glass-transition temperature (T_g)

A differential scanning calorimeter (DSC-60, Shimadzu Co., Ltd., Kyoto, Japan) was used to determine the T_g values of all of the samples. An empty pan was used as a reference. The samples were weighed into an aluminum pan, then placed in the heating chamber of the DSC instrument, and heated from 10 to 200°C at a rate of 10°C/min. Before each run, a baseline was constructed with an empty aluminum pan over the temperature range 10–200°C at a rate of 10°C/min. The samples were then heated at the same rate to 200°C, and the procedure was repeated.

MDSC

The thermal properties of all of the samples were also investigated with the help of MDSC. Samples were analyzed by MDSC according a previously described procedure.[21,22] The samples were weighed into an aluminum pan, then placed in the heating chamber of the MDSC instrument, and heated from 20 to 200°C at a rate of 1.5°C/min; the amplitude and the period of the MDSC instrument were 1.5°C and 90 s, respectively. Before each run, a baseline was constructed with an empty aluminum pan over the temperature range 20–200°C at a rate of 1.5°C/min. The samples were then heated at the same rate to 220°C, and the procedure was repeated. The

resulting heat flow thermograms were analyzed to determine the thermal properties of the samples. Samples (5–10 mg) were scanned in hermetically sealed MDSC aluminum pans.

RESULTS AND DISCUSSION

The commercial starch samples used in the spray-drying experiments and their formulations are summarized in Table I.

Moisture contents

Both commercial native cornstarches had similar moisture contents, that is, 12.69 and 12.67% for Am-rich and waxy cornstarch, respectively. These values were significantly higher than the water contents of the spray-dried TPS samples. The moisture contents for the latter were in the range 4.8–5.5% for the TPS samples spray-dried from solutions and between 5.9 and 6.2% for samples obtained from dispersions. The moisture contents of the powder mostly depended on the drying conditions and the solid contents in the solution. Therefore, the drying conditions and solid contents were kept constant for all samples.

Variations in Am and Ap ratios did not affect the moisture contents of the spray-dried TPS blends. Spraying from solution versus spraying from dispersion seemed to result in a small difference in the moisture contents. This could be explained by a lower moisture diffusion rate for the highly crystalline granules in the dispersions. As previous studies showed, the presence of water allowed Am–Am interaction over time, and because of the larger free volume, water could be arranged in the crystalline matrix.[6] Earlier studies also showed that the net matrix crystallinity was increased with increasing water activity of gelatinized starch samples.[23] High diffusion rates and low moisture contents in the end product could help to minimize the retrogradation of TPS blends and produce amorphous TPS films in the future.

Morphology

Figure 1 shows the granular morphology of the commercial and spray-dried powder samples.

The high-Am-N cornstarch showed a mixture of rounded granules from the floury endosperm and angular granules from the horny endosperm.[24] The native maize starch showed angular granules, usually having four or five sides. In general, the Am-rich starch granules were rough, with different particle shapes; the surface of the Ap-rich granules seemed smoother.

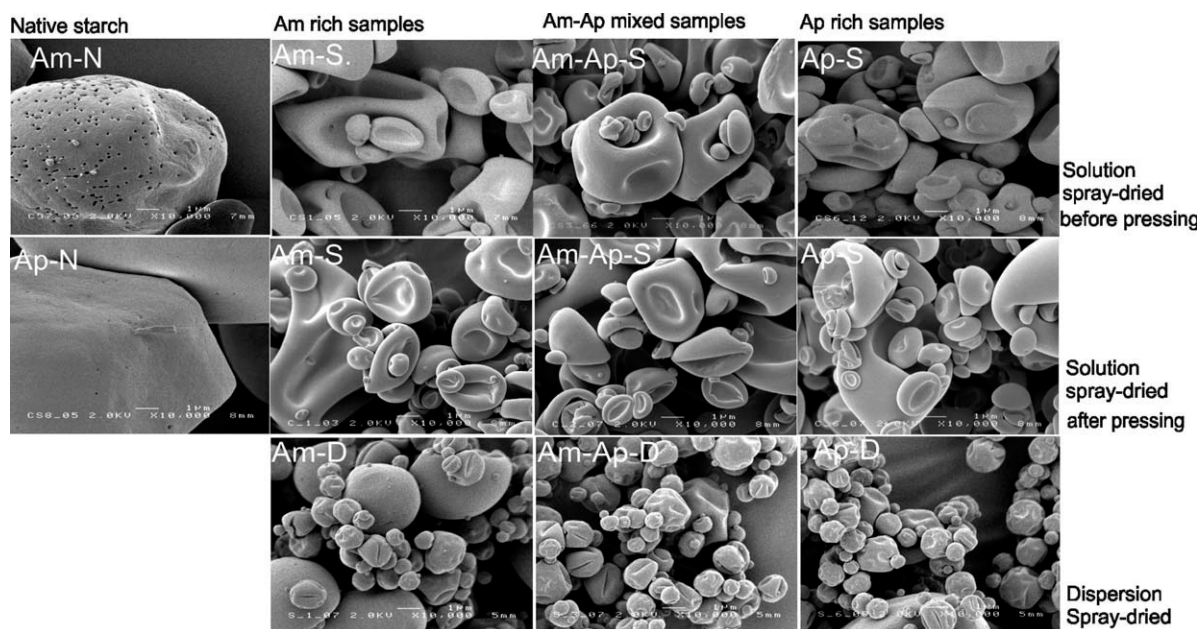Solution spray-dried TPS samples showed significantly different morphologies. All of the samples

Figure 1 Morphology (SEM) of the dried product. Left column: Commercial samples. Top and middle rows: Samples dried from the solutions before and after pressing; Bottom row: Samples dried from dispersions.

showed irregular, shriveled, and cratered particles without any smooth or angular ones, and agglomeration levels were high. To test for the presence of hollow particles, the spray-dried powder samples were compressed in tableting equipment. A pressure of 5 bars was applied for 1 min, and SEM images were recorded (see Fig. 1, middle set). This treatment did not show any broken or hollow particles.

The Am-rich granules showed brightness on the edges of the craters. One possible explanation for this phenomenon was previously reported[25] and suggested that the Am content was higher at the hilum for Am-rich corn samples.[24,25] The higher density of the hilum Am-rich sample led to brightness. Another possible explanation might have been the different microstructures of the hilum in granules.

Samples obtained from the dispersed spray-dried granules were more regular, with only a small fraction of shriveled particles, which supposedly are formed from truly dissolved material. As for native samples, the high-Ap maize starch had smoother and more regular granules compared to the high-Am samples. The mixture showed characteristics of both starches, that is, regular and irregular. The degree of agglomeration within the set of dispersion-based samples was similar but clearly lower than that found for the solution-based samples.

Crystalline structure

The crystalline nature of the spray-dried product depended on the properties of the feed material and on the drying conditions.[26] The state of matter (amorphous vs crystalline) is very important for stability and utilization in many domains, for example, the food or pharmaceutical industries.[27] On the basis of XRD, the starches could be classified into three groups: A-, B-, and C-type starches.[28] Am and Ap are packed into granules that are partly crystalline and partly amorphous in structure. From previous research, it has been proven that the crystalline part consists of parallel, left-handed double helices from the short chain of Ap.[29,30] The density of A is higher than that of B.[31] There was also reported another type of starch polymorph, C type, which is a combination of the A- and B-type polymorphs. The B-type polymorph is found in the center of the granule, and the A-type polymorph surrounds the B-type. Further research is needed to determine whether the amorphous region of the C-type starch granule consists of A- or B-type polymorphs or a mixture of both.[32]

The XRD patterns of all of the samples are shown in Figure 2. Previous research indicated that native samples contain both A-type (high-Ap starch) and B-type (high-Am starch) crystals before treatment and that the degree of crystallinity decreases with an increase in the Am content.[2,24,33,34]

All of the samples obtained from solution spray drying showed a noncrystalline pattern. Compared to the native materials, a significant change in the crystallinity was observed. The samples became totally amorphous, even for high-Ap starches. This result was in strong contrast to that of previous work that showed that the degree of crystallinity increased slightly with an increase in the Am content for the solution heat treatment of starches.[33–35] This difference
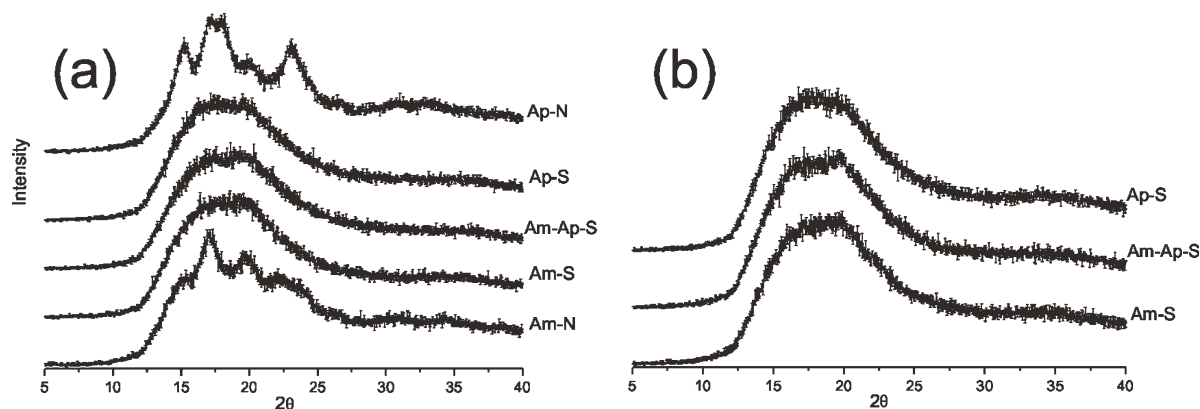
Figure 2 XRD patterns of the cornstarch solution-dried product: (a) immediately after production (native samples used as a reference) and (b) after 2 months of storage under dry conditions.

could be explained by the fast solidification and cooling of the dissolved starch, which inhibited crystallization and produced amorphous materials. This also explained why the Am/Ap ratio did not show any effect on the product crystallinity after the solution spray drying of the TPS blends. The results were remarkable, as it has been reported that maltodextrin enhances the crystallization of Am/Ap blends.[6]

The amorphous nature of the obtained samples was maintained during storage of the samples under dry conditions in a desiccator for 2 months. (The stability of these materials under humid conditions was part of another study). After 2 months, the samples were checked again by XRD [Fig. 2(b)], and the X-ray patterns of all samples were the same as before; this indicated good stability under these conditions.

Similar to the spray drying of solutions, the dispersed starches were dried and evaluated by X-ray analysis. The results are shown in Figure 3, which shows that the crystallinity decreased by a small amount, but the samples retained their typical diffraction patterns. The Ap sample still possessed an A-type diffraction pattern, and the Am sample had a B-type pattern. The crystallinity of high-Ap starch was much higher than that of the Am-rich sample. The dispersion-dried amylose–amylopectin (Am–Ap-D) mixture showed patterns of both Am and Ap diffraction.

This XRD analysis proved that the amorphous nature of the solution-dried TPS samples was not caused by the spray-drying technique but was related to the use of true TPS solutions. From this, we concluded that spray drying from solutions could be a useful technique to produce amorphous TPS feedstocks containing different Am/Ap ratios for the manufacturing of starch films with low moisture contents.

PSD

The most important physical parameters of powders are PS and PSD. These properties determine the transport and flow of powder in equipment and its

compaction and segregation behavior. In addition, these properties play an important role in the food industry, such as in TPS films, and affect the aroma, texture, and appearance.[36,37] A decrease in PS increases the particle surface area, causes greater affinity for moisture, and increases the risk of agglomeration during the drying process.[38] Figure 4 shows the density distribution of the spray-dried powders and the native granules.

The high-Am-N cornstarch and maize starch [Fig. 4(a)] showed X_{90} is defined as 90% of Starch granules, respectively. The maize starch contained the largest particles among all of the samples. It was interesting to note that there was a fraction of spherical granules in the high-Am-N cornstarch that had PSs bigger than the Ap granules.

In solution drying [Fig. 4(c)], a bimodal and skewed distribution was observed for all TPS samples with two different peaks; this indicated two predominant sizes. Stickiness and a high rate of agglomeration could be the reason for this distribution. Because of the stickiness, bridges formed between smaller particles, and consequently,
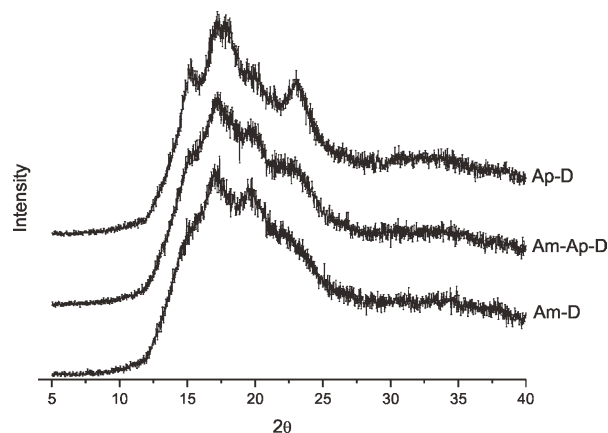

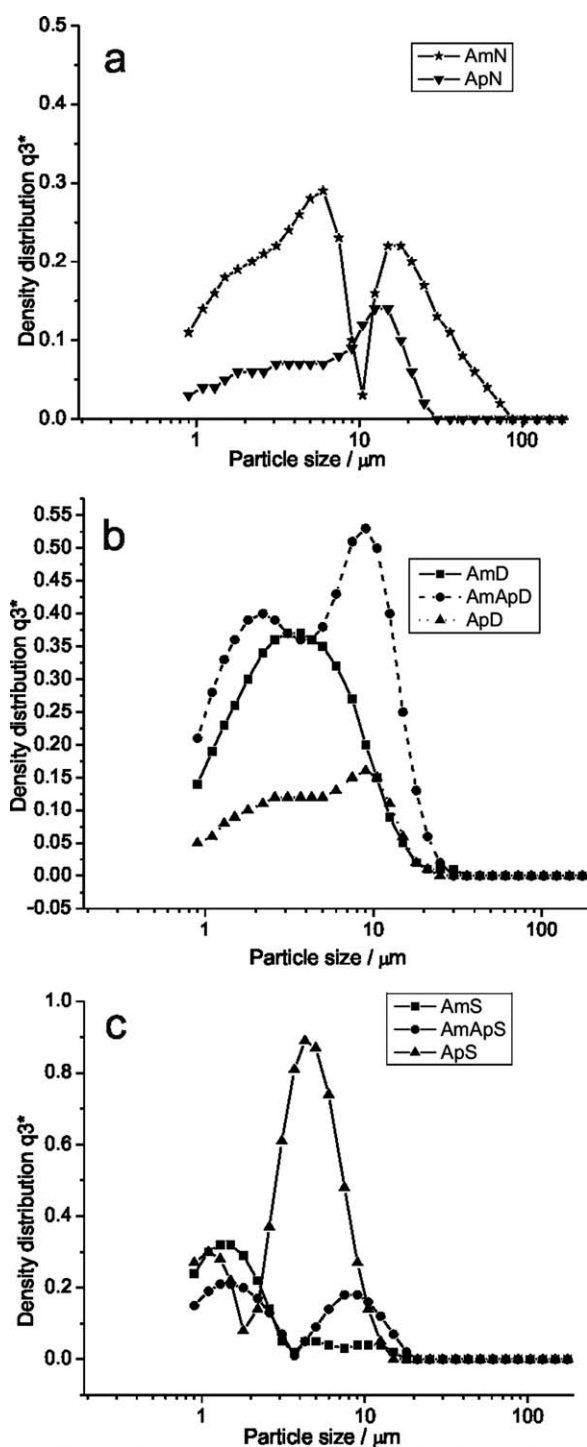**Figure 3** XRD pattern of the dispersion-dried product.

Figure 4 Density distributions of all powder samples: (a) native, (b) dispersion-dried, and (c) solution-dried samples.

agglomeration occurred, which increased the particle diameter. Therefore, the first peaks corresponded to the minor particles, and the second peaks corresponded to the agglomeration of these and resulted in larger diameters. The cumulative distribution showed that all of the solution spray-dried samples had the same PS and an X_{90} percentile of less than 7 μm.

However, the dispersion-dried samples [Fig. 4(b)] were in ranges of 13 and 19 μm for the high Am and the high Ap, respectively, and the high-Am maize starch dispersion [dispersion-dried amylose (Am-D)] showed a unimodel distribution. This was understood because PS (X_{90} percentile) is a function of the feed PS, concentration, and composition. The PS of the dispersion-based samples was higher than that of the solution-based samples and was proportional to the molecular composition. The higher the molecular weight of the feed was, the higher the PS was. The solution-dried samples did not follow this pattern, and all of the samples had the same PS (X_{90} percentile). In previous research, it was observed that in dispersion spray drying, PSD mostly depended on the inlet temperature, aspirator speed, and feed concentration.[9,39] The cohesiveness of dispersion-dried samples was lower than that of solution-dried samples. A lower cohesiveness and a higher crystallinity decreased the rate of agglomeration of the dispersion-dried samples.

Given that small starch particles perform best as fillers in linear low-density polyethylene films,[37] the spray-drying technology may also a beneficial pathway for making starch filler and improving the mechanical properties of synthetic film materials.

Powder flow properties

Bulk density

All industrial operations in handling powders depend on flow characteristics. They play a role in industrial operations such as mixing, transportation, and packaging.[17] Bulk density is used as an indicator and relates to the morphology and crystallinity of powders. A higher bulk density is connected with better powder flow. The bulk density data are collected in Figure 5.

Only native powder samples showed bulk densities above 5.50 g/mL, and all of the dried samples had low bulk densities, with solution-dried samples having the lowest. The shriveled and cratered structures of the particles and the amorphous nature of the latter powders explained the low bulk densities. When we compared the data of the native materials and the ones obtained for the samples obtained from solution and dispersion, it was evident that spray drying from solution significantly lowered the bulk density of the powders.

Tap density and flow properties

According to previous work, low CIs and low HRs are good indicators for the flow properties of a material.[17,40] This is in accordance with the density measurements. CI is a measure of powder bridge
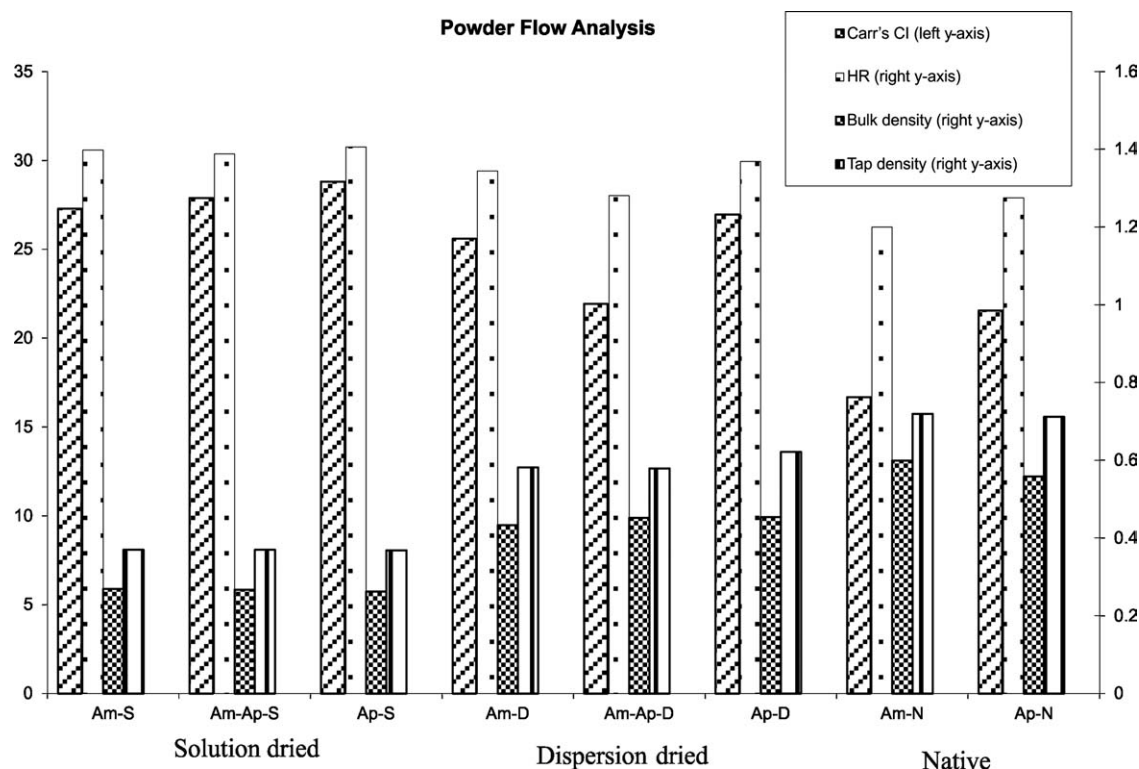
Figure 5 Graphical representations of the HR, Carr's CI, and bulk and tap densities.

strength and stability, and HR is a measure of the interparticulate friction. A Carr's CI of less than 10 or an HR of less than 1.11 is considered to provide excellent flow. On the other hand, a CI of greater than 38 or an HR of greater than 1.60 is considered to provide very poor flow. Depending on the values measured for these indicators, powders can be classified as having good, fair, passable, or poor flow. The flow potential of a powder increases by compression by tapping. The values for HR, Carr's CI, and tap density are plotted in Figure 5.

The tap densities of all of the samples were low and in line with observed low bulk densities. The high-Am-N corn and maize starches showed fair and passable flow properties, respectively, according the CI and HR classification.[17] On the basis of the results obtained, the flow properties of all of the solution spray-dried samples were rated as poor on the basis of their CI and HR values. The difference between the tap and bulk densities showed that the samples were irregular and had high porosity.

The dispersion-dried samples had tap densities that were higher than those of the solution-dried ones but were lower than those found for the native starches. The dispersion-dried samples of high-Am starch and the mixture of Am and Ap were also rated with passable flow. The high-Ap sample was classified as a poorly flowing material. The moisture contents, morphology, and nature (amorphous and crystalline) of powders are known to influence the

bulk material properties.[41] Spherical and regular particles with large PSs have better flow properties than irregular and smaller ones.[40] As we already have seen for the solution-dried samples, the morphology was irregular and shriveled; this clearly led to low bulk densities and poor flow characteristics.

Isothermal and isobaric treatment

The loss in birefringence was studied under constant pressure and temperature conditions. The degree of gelatinization of starch was analyzed with polarized light microscopy to observe disrupted granules and the loss in birefringence. This method has been used by several authors and has been found to be suitable for detecting very low degrees of starch gelatinization.[18,19,42–44]

Figure 6 shows the results of loss of birefringence for all of the TPS samples in the sequence of no treatment, isothermal treatment, and isobaric treatment, respectively (in the columns from left to right). Am-N and native amylopectin (Ap-N) were the native samples of high-Am maize starch and normal cornstarch, respectively. Ap-N was completely gelatinized after the isobaric treatment and lost its characteristic Maltese cross of polarized light refraction. The swelling level and average PS of the high-Ap samples were higher than those of the Am samples. The high-Am maize starch samples showed different results. The swelling rate and degree of
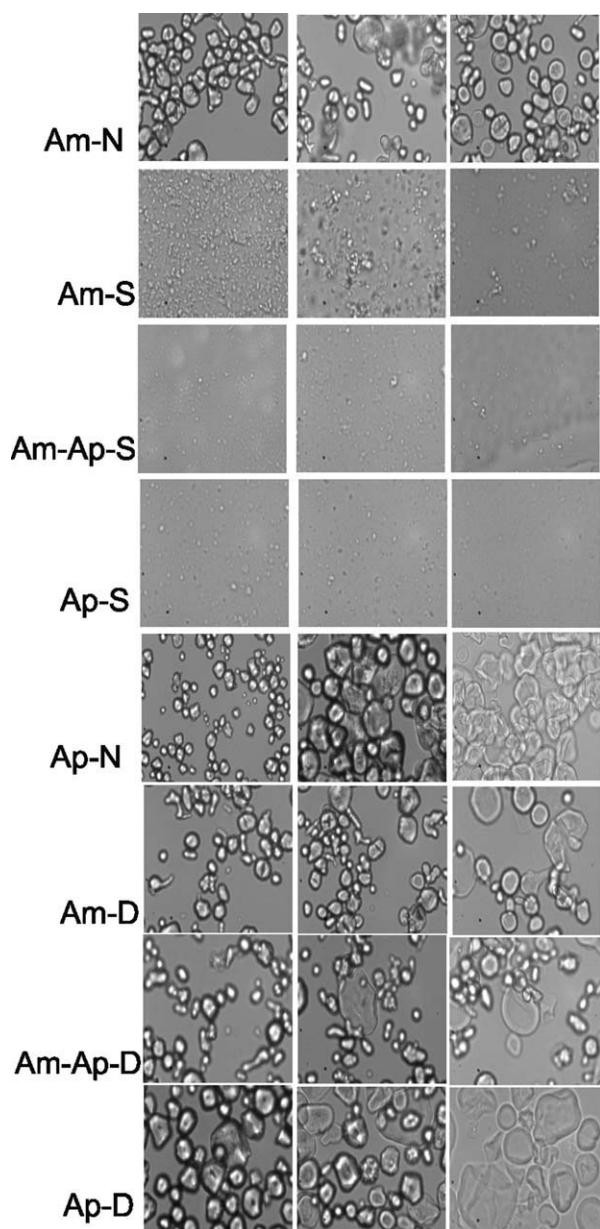
Figure 6 Loss of birefringence for the starch samples. Left column: Untreated sample. Middle column: Isothermally treated sample. Right column: Isobarically treated samples.

gelatinization were low, even after isobaric treatment. These results were in agreement with the results presented before.[18,19,45] The solution-dried samples and dispersion-dried ones showed quite different results. The PS of the solution-dried samples was small, and the samples showed hardly any birefringence. The low average PS and the amorphous nature of the solution-dried samples are expected to give better results in the preparation of films from starch/polymer blends.

It also should help to improve the mechanical properties, such as tensile strength, yield strength, and percentage elongation, of biofilms produced

from starch blends. The amorphous nature results in a better mixing of polymer blends.[46–48] The dispersion-dried samples showed results similar to those of native materials. The dispersion-dried amylopectin (Ap-D) content was totally gelatinized after isobaric treatment, whereas the Am-D still showed some granules with birefringence.

Viscosity

The viscosities of all of the samples were determined with a Brookfield DV-II viscometer (DV II, Middleboro, MA 02346, USA), and the data are shown in Figure 7. The viscosity of all samples varied significantly; for dispersed and native materials, they depended on their Am/Ap contents. At the same time, a striking difference was observed for the solution-based spray-dried samples; that is, the measured viscosities were significantly lower than those found for the other materials and were independent of the Am/AP ratio.

These results were found to be reproducible in multiple measurements and could be explained by a difference in the degree of solubilization and particle disintegration.[20] This interpretation of the observed viscosity data was supported by the results shown in Figure 6. From this, it was evident that the solution spray-dried materials were highly solubilized under the conditions of viscosity measurement, whereas the native and dispersed samples still showed a high degree of granular retention and gelatinization. Likewise, as shown in Figure 6, the granule size and degree of gelatinization could be correlated to the viscosity data in Figure 7; that is, gelatinized larger particles resulted in higher viscosity levels as long as the granules or particles were not fully disintegrated.
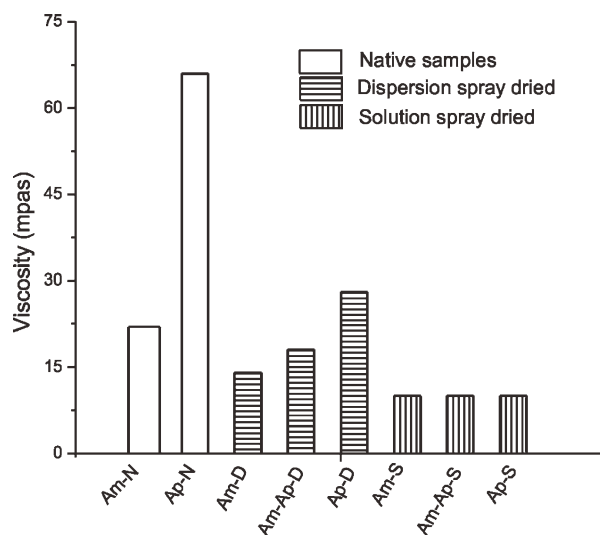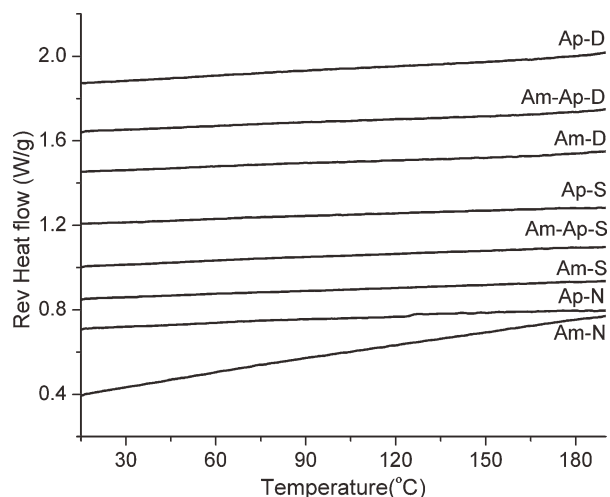

Figure 7 Viscosity of the starch powder samples.

Figure 8 MDSC curves of the all spray-dried samples. Rev.: Reversible.

T_g

DSC and MDSC were used to observe variations in the glass-transition point for the compositions. The DSC results show that the thermograms were all identical and gave no conclusive information about the T_g values of the materials.

In MDSC, the following equation was used to describe the total heat flow between the sample and the reference:[21,22]

$$\frac{dQ}{dt} = C_P b + f(T, t)$$

where dQ/dt is the resultant heat flow, C_P is the heat capacity of the sample, b is the rate of temperature change, and $f(T,t)$ is the heat flow from kinetic processes. In MDSC, the total heat flow and the two individual components can be distinguished as the heat-capacity component ($C_P b$), or reversing heat flow, and the kinetic component $f(T,t)$, or nonreversing heat flow. The glass transition is detected in the reversing heat flow, as it is related to the sample heat capacity, whereas in nonreversing heat flow, processes such as enthalpic relaxation, crystallization, evaporation, or decomposition are resolved.[21,22]

Previous research has shown that T_g is greatly affected by the moisture content; therefore, we determined the thermal profiles using an open pan, allowing water evaporation and measurement of the dry T_g.[21,22]

The MDSC heat flow curves are shown in Figure 8. The results focus on the glass transitions of the spray-dried samples. None of the samples showed any T_g that could be attributed to the intermolecular and intramolecular hydrogen bonds between the starch chains and, thus, limit chain movement.[3]

In summary, it can be stated that spray drying affected the morphology, PS, surface structure, and

gelatinization of starch but did not affect the T_g values of the starches. Solution spray drying can be helpful in the production of amorphous TPS films for food packaging.

CONCLUSIONS

The properties of solution- and dispersion-dried TPS samples of maize starch with different Am-to-Ap ratios were systematically studied before and after spray drying. TPS samples obtained from solution showed totally different properties compared to those obtained from dispersion. The Am-to-Ap ratio did not have any effect on the solution-dried samples. Most properties, such as moisture content, crystallinity, PSD, viscosity, and flow properties, were similar for all of the solution-dried TPS materials. All samples were amorphous in nature with low average PSs, low moisture contents, and viscosities, and the variation in the molecular weight distribution introduced by the blending of Am and Ap did not have any effect on these properties. Because of these properties, the solution spray drying of TPS powder can be a useful technique for producing improved amorphous thin TPS films with different plasticizers. This technique produced TPS powders with low moisture contents, narrow distributions, and amorphous material and, thus, could play an important role in the production of thin TPS films with better mechanical properties and different retrogradation behaviors.

On the other hand, the samples obtained from dispersions remained crystalline, and the PSD and viscosities increased in line with the composition of the formulations. Although the morphologies of the solution-dried samples were irregular and shriveled, the dispersion-dried materials still resembled the original native material structures. Flow indicators based on the bulk and tap density measurements of all of the processed powder samples pointed to quite poor powder flow characteristics. All of the samples, regardless of method, did not show any T_g because of intramolecular and interhydrogen bonding among starch chains.

Retrogradation behavior and the use of low-molecular-weight plasticizers will be investigated in the next part of our study to manufacture TPS films.

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