Amylose-Lipid Complex Formation During Single-Screw Extrusion of Various Corn Starches'

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Commercial corn starches containing 0-70% amylose were extruded
with and without various lipids (myristic, stearic, and behenic acids; mono-
glyceride Dimodan PV; and tristearin) in a single-screw laboratory
extruder at 11

Extrusion cooking is a popular unit operation for producing a variety of food products with numerous ingredients requiring a wide range of processing conditions. Typical feedstocks include starch, protein, lipids, water, and additives. In general, extrusion of starchy foods results in gelatinization of starch, denaturation of protein, and formation of complexes between starch and lipids and between proteins and lipids (Mercier and Feillet 1975, Mercier et al 1980, Colonna and Mercier 1983, Ho and Izzo 1992). The complexes between starches and lipids are due to the ability of the amylose fraction of starches to bind lipids such as fatty acids. This ability of amylose to form complexes with a wide range of polar and nonpolar organic compounds is currently used to fractionate amylose from amylopectin (Mercier et al 1980). Amylose complexes are generally prepared by adding a complexing agent to a hot aqueous solution of starch. With an extruder, however, this can be achieved momentarily and at low moisture contents.

Complex formation during twin-screw extrusion cooking has been studied by Mercier et al (1979, 1980), Colonna and Mercier (1983), Schweizer et al (1986), Galloway et al (1989), Guzman et al (1992), Ho and Izzo (1992), and Strauss et al (1992). Mercier et al (1979, 1980) reported that twin-screw extrusion cooking of manioc, potato, and corn starches in the presence of native lipids or added saturated and unsaturated fatty acids containing 12-20 carbon atoms, glyceryl monostearate, and sodium stearoyl lactylate resulted in the formation of V-amylose complexes. Water solubility and susceptibility of the starches to α -amylase digestion both decreased upon formation of the complexes.

Formation of complexes during twin-screw extrusion cooking of corn starch and glyceryl monolaurate was confirmed by Stute and Konieczny-Janda (1983) by using differential scanning calorimetry. In a similar study, Schweizer et al (1986) found that the addition of oleic acid to wheat flour, before extrusion, decreased also an inverse relationship between the degree of α -amylase digestion and the amount of complexed starch. Galloway et al (1989) studied the properties and structure of amylose-glyceryl monostearate complexes formed in solution or upon twin-screw extrusion of wheat flour and reported decreases in starch solubility,

tions of the extrudates were determined. Additions of fatty acids and
monoglyceride resulted in V-patterns in X-ray diffractograms and
decreased iodine-binding capacity of the extruded starches, indicating
decreased iodine

water-holding capacity, enzyme susceptibility, and degree of ex-
pansion of the extrudates.
Except for the work of Mercier et al (1980), most of the work

on amylose-lipid complex formations during extrusion cooking has been reported only for a limited range of lipids and with wheat flour or manioc starch. No systematic study has been reported on the effects of different categories of lipids on properties such as expansion ratio, bulk density, water-solubility index, and water-absorption index of different qualities of starch. No attempt
has been made to correlate the effect of increasing degree of complexing to physico-chemical properties of extruded starches. Therefore, this study was undertaken with the objective of studying complex formation during single-screw extrusion cooking of starches with lipids, and the effect of degree of complexing on selected physico-chemical properties of extruded starches.

MATERIALS AND METHODS

Materials
Commercially available 0, 25, 50, and 70% amylose corn starches used in this study were received gratis from American Maize-Products Co., Hammond, IN. Their chemical compositions, as supplied by the manufacturer, are given in Table I. Five different lipids were used. Myristic (tetradecanoic), stearic (octadecanoic), and behenic (docosanoic) acids were received gratis from Humko Chemical Division of Witco Corp., Memphis, TN. Dimodan PV, a monoglyceride based on soybean oil with 70-95% C18 and 5-30% C16, was received gratis from Grindsted Products, Inc., Industrial Airport, KS. The triacylglycerol tristearin was purchased from Sigma Chemical Co., St. Louis, Mo. A lipid substitution level of $\frac{4}{\sqrt{6}}$ (dwb of starch) was used for all samples. Starches were granulated by spraying water on a inclined rotating pan before extrusion and were preblended with lipids and distilled water in a Hobart mixer for 2 min to achieve desired lipid and moisture contents.

TABLE I Proximate Analyses of Various Corn Starches

	Starch Amylose Content (%, dwb)			
	0	25	50	70
Protein $(g/100 g)$	0.2	0.3	0.5	0.8
Phosphorus $(mg/100 g)$	4.2	14.2	22.8	19.1
Fat $(g/100 g)$	0.1	0.1	0.4	0.3
Ash $(g/100 g)$	0.1	0.2	0.1	0.1
Moisture $(g/100 g)$	10.6	9.5	11.0	10.6

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Extrusion

A laboratory extruder (model 2802, C.W. Brabender, Inc., South Hackensack, NJ) with a 1.9-cm barrel diameter and a 20:1 barrel length-to-diameter ratio was used. The extruder screw had a compression ratio of 3:1. The temperatures of the die and the compression sections of the extruder were set at 110° C; the feed section was held at 70° C. The extruder was fed full while keeping the screw speed constant at 110 rpm.

For physico-chemical analyses, extrudates were dried at 40° C in a convection air-dryer and were ground in a Powdertec 3090 micro-mill (Tecator, Inc., Silver Spring, MD) to pass through a 50-mesh sieve. All the ground samples were defatted in a Soxtec fat-extractor with petroleum ether at 37° C (bp 34.6° C) to remove uncomplexed lipids before physico-chemical analyses. In the fatextractor, the petroleum ether was indirectly heated by mineral oil at 96° C.

X-ray Diffraction

Complex formation between the starches and lipids during extrusion was studied by using powder X-ray diffraction. All starches were defatted with petroleum ether in a fat-extractor (as described earlier) to remove free lipids, and dried at 40° C to 12% moisture in a vacuum oven. Samples of native starch, extruded starch, and starch extruded with lipids were analyzed with an X-ray diffractometer (Pad V, Scintag, Inc., Sunnyvale, CA) equipped with a graphite monochrometer and a scintillation detector. The X-ray source was $CuK₀$ radiation with a wavelength of 1.5406 $^{\circ}$, 40 kV, and 30 mA. Data were collected from 0-35 $^{\circ}$ 20 (θ being the angle of diffraction) with a step width of 0.02° and step time of 0.4 sec. Value of 2θ for each identifiable peak on the diffractograms were estimated, and crystal d -spacings were calculated using Bragg's law.

Iodine-Binding Capacity

The iodimetric method of amylose content determination of Schoch (1964) was used with one modification to determine the iodine-binding capacity (IBC) of the native and extruded starches. Before IBC analysis, the samples were defatted by using petroleum ether (bp 34.6° C) to remove free lipids. The bound lipids were not removed, and residual IBC was determined. Complexed starch was calculated as outlined by Robinson et al (1983), Schweizer et al (1986), and Rutschmann and Solms (1990).

$$
Complexed\;start\;(\%) = \frac{(IBC_{native\;starto} - IBC_{complexed\;starto})}{IBC_{native\;starto}} \times 100
$$

Iodine Spectra of Starch Samples

A modified method of Sowbhagya and Bhattacharya (1971) was used to determine the iodine spectra of extruded starches. Starch samples were solubilized in $1N$ KOH instead of $1N$ NaOH as recommended by Schoch (1964). The absorbance spectra of starch-iodine complexes were measured using a spectrophotometer (DU 60 Beckman) from 400-700 nm, and wavelength of maximum absorption (λ_{max}) values were determined. The ratios of absorbances at 630 and 520 nm for amylose and amylopectin, respectively, were also reported.

Expansion Ratios

The radial expansion ratios of the starch extrudates were calculated by dividing the average cross-sectional areas of the extrudates by the cross-sectional area of the nozzle. Each value was an average of 10 readings.

Bulk Density

The bulk densities of the extrudates were calculated as:

$$
\rho = 4/(\pi \times D^2 \times L)
$$

where $\rho =$ bulk density (kg/m³), $D =$ diameter of the extrudate, and $L =$ length of 1 kg of extrudate.

Water-Soluble Carbohydrates

Water-soluble carbohydrates were determined as described by Sokhey and Chinnaswamy (1992). Total carbohydrate content of the starch solution was determined by the phenol sulfuric acid method (Dubois et al 1956).

Water-Solubility Index and Water-Absorption Index

Water-absorption index is the weight of the gel obtained per gram of dry sample. Water-solubility index is the amount of solids recovered by evaporating the supernatant from the water-absorption tests, expressed as percentages of dry solids in the sample. These were determined by the procedure outlined by Anderson et al (1969).

RESULTS AND DISCUSSION

Addition of 4% lipids to starches before extrusion resulted in formation of complexes between the amylose and all lipids, except for tristearin. The presence of complexes was confirmed by Xray diffraction, IBC, iodine spectra of the starch solution, and ratio of absorbances at 630 and 520 nm.

X-Ray Diffraction

The X-ray diffraction study was performed to obtain qualitative evidence of complex formation. The powder X-ray diffractograms of 25% amylose starch extruded with lipids are shown in Figure 1. For native starch, strong peaks were observed at 2θ values of 15.1, 16.4, 17.5, 18.7 and 22.6 A, corresponding to d -spacings of 5.95, 5.39, 5.2, 4.7, and 3.9 A, respectively. This pattern closely matches reported values for A-type cereal starches (Zobel 1964, 1988).

Upon extrusion cooking of starch, the X-ray diffraction pattern changed to a V-hydrate form. This was indicated by a small peak at 2θ of 7.3 A. Zobel (1964, 1988) reported that such a peak often appears as the first indication that V complexes have been formed. Other peaks, located at 2θ of 12.7 and 19.8 A, were not observed in native starch, indicating that extrusion resulted in formation of complexes between starch and native lipids. Charbonniere et al (1973), Mercier et al (1979, 1980) and Chinnaswamy et al (1989) reported similar results.

Upon extrusion of starch with fatty acids and monoglyceride, the size of the peaks at 7.3, 12.7, and 19.8 A depended on the type of lipid. The heights of these peaks increased as the fatty acid chain length decreased from 22 (behenic acid) to 14 (myristic acid), suggesting an increasing degree of complex formation. Figure 2 shows the X-ray diffractograms of starches with different amylose contents extruded with myristic acid. For all complexing lipids, the greatest peak heights were obtained with 70% amylose

A A $W_{\rm{max}}$ 10 15 20 25 30 35 20

Fig. 1. X-ray diffractograms of 25% amylose corn starch. Native starch (A), extruded starch (B), starch extruded with tristearin (C), monoglyceride Dimodan PV (D), and behenic (E), stearic (F) and myristic (G) acids.

starch. No evidence of complex formation was observed with waxy starch. The peak heights for V-type patterns increased with increasing amylose content; maximum peak heights were observed for 70% amylose starch. Sievert and Holm (1993) also showed the linearity between amylose content of starch and enthalpy of lipid-amylose complex melting. However, they used differential a direct relationship between the amount of complexing and the peak heights in the X-ray diffraction studies. This needs further investigation. Starch extruded with tristearin gave the same Vtype pattern as starch extruded without added lipids, which would suggest that the complexing was between the starch and native lipids rather than between the starch and the tristearin. Similar results were reported by Osman et al (1960) with some triglycerides and soybean oil.

IBC

Figure 3 shows the IBC of starches extruded with lipids. The IBC is significantly different for different starches $(P > F 0.0001)$ as well as for different lipids $(P > F 0.0001)$. The formation of complexes reduced the IBC of the starches. As any free fatty acid present in the samples had already been removed, any reduction in the IBC was attributable to the unavailability of the iodine-binding sites because of lipid-binding during extrusion. Thus, these results confirm the results of X-ray diffraction.

IBC was not significantly affected by addition of tristearin to the starches $(P > F 0.9398)$. This is shown in Figure 3 where the two curves are superimposed on each other. As discussed above, the X-ray diffractograms for starches extruded with tristearin and starches extruded without added lipids were also similar. For all levels of amylose content, the lowest IBC was observed with myristic acid (carbon chain length of 14). These values were significantly different than those observed for all other lipids. In X-ray diffractograms, maximum peak heights were also observed for starches extruded with myristic acid, indicating maximum complexing compared to all other lipids. Hahn and Hood (1987) reported maximum binding with stearic acid (C18). Lagendijk and Pennings (1970) and Hoover and Hedziyev (1981) found maximum binding with monoglyceride of myristic acid. However, neither study used extrusion to form the complexes.

Addition of the monoglyceride Dimodan PV also decreased the IBC of starches that were significantly different from the control, tristearin, and behenic acid, but not significantly different from stearic acid.

Table II compares results obtained in this study with results of similar studies reported in the literature. Table II also gives percentages of complexed starch based on IBC values for native starches and residual IBC of starches extruded with different lipids. The IBC of native 25, 50, and 70% amylose content starches

Fig. 2. X-ray diffractograms of 0, 25, 50, and 70% amylose starches extruded with myristic acid.

Fig. 3. Iodine binding capacities of extruded corn starches as a function of lipid type and starch amylose content.

Starch	Type of Lipid	Extruder Conditions	IBC (mg/100 mg)	Complexed Starch $(\%)$
Corn starch $(25\%$ amylose) ^a	Native starch	Single screw	3.60	\cdots
	No lipid added	110° C	3.49	3.0
	4% Myristic acid	110 rpm	1.73	52.0
	4% Stearic acid		2.11	41.0
	4% Behenic acid		2.87	20.0
	4% Dimodan		2.42	33.0
	4% Tristearin		3.46	3.9
Manioc starch $(17\% \text{ amylose})^b$	Native starch	Twin screw	3.50	\cdots
	No lipids added	200° C	3.60	\cdots
	2% copra	40 rpm	3.40	2.9
	4% copra		3.50	0.0
	2% Dimodan		3.40	2.9
	2% oleic acid		3.30	5.7
Wheat flour ^c	No lipids added	Twin screw	Not reported	32.0
	2% Soya oil	156° C		35.0
	1% Linoleic acid	200 rpm		88.0

TABLE II Comparison of Iodine-Binding Capacities (IBC) of Starches Extruded with Various Lipids

^a Data from this study.

^bData from Colonna and Mercier (1983).

'Data from Schweizer et al (1986).

were 3.6, 6.8, and 10.5 mg/ 100 mg of starch, respectively. The IBC of amylopectin was assumed to be zero. Based on amount of initial amylose content, as much as 50% of the amylose present in these starches was complexed with lipids. Starches extruded with no added lipid showed as much as 3% complexing, which may be attributed to the complex between native lipids present in commercial-grade starches (Table I).

Our IBC values and percentages of complexed starch were different than those observed by Colonna and Mercier (1983) and Schweizer et al (1986) because they used different lipids, starches, and extrusion process conditions to form the complexes (Table II). It appears that the amount of starch that can complex with lipids depends on the processing conditions and type of lipid.

Iodine Spectra of Starches

To confirm the formation of complexes, λ_{max} for native starches and for starches extruded with and without lipids were also determined. Native waxy starch showed λ_{max} at 530 nm, whereas native starches and starches extruded without lipids showed λ_{max} at 594-603 nm for amylose contents of $25-70\%$. For starches extruded with fatty acids and monoglyceride, λ_{max} was observed at 590, 593, and 594 nm for behenic acid; 584, 586, and 591 nm for stearic acid; 568, 575, and 585 nm for myristic acid; and 577, 584, and 588 nm for Dimodan PV (25, 50, and 70% amylose starches, respectively). Thus, the absorption maxima shifted towards the amylopectin side, indicating formation of complexes. The iodine spectra of starches extruded with tristearin had λ_{max} values similar to those observed for starches extruded without lipids (595, 599, and 605 nm for 25, 50, and 70% amylose starch), indicating that tristearin did not form complexes with starches.

Changes in the ratio of absorbance of iodine-polysaccharide complexes at 630 and 520 nm, the λ_{max} for amylose and amylopectin, respectively, are indicative of a change in the composition of linear or branched fractions of the starch molecules (Sokhey and Chinnaswamy 1992). The 630/520 ratios for all the starches extruded with and without lipids are shown in Table III. Extrusion of starches without added lipids did not affect the 630/520 ratios. However, extrusion of starches with fatty acids and Dimodan PV decreased the 630/520 ratios. The addition of tristearin, on the other hand, had no significant affect on the 630/520 ratios.

The changes in the absorbance ratios can be explained as decreases in the availability of the linear fraction of starch to bind with iodine due to complex formation with lipids. These results are consistent with other findings in this study and indicate that iodine spectra and ratio of absorbances at 630 and 520 nm can also be used to detect the formation of complexes during extrusion cooking.

Effect of Complex Formation on Physico-Chemical Properties of Starches

The effects of amylose-lipid complex formation on the physicochemical properties of 25, 50, and 70% amylose starches extruded with lipids are shown in Figures 4-6. As the amount of complexed amylose increased, the expansion ratios and the percent of watersoluble carbohydrates decreased, and the bulk densities increased. These properties reached limiting values as the fraction of available

TABLE III Effect of Lipids on 630/520 Ratio^a Values of Native and Extruded Starches

Sample	Starch Amylose Content (%, dwb)				
		25	50	70	
Native	0.6	1.3	1.5	1.6	
Extruded	0.6	1.3	1.5	1.7	
Behenic acid	0.6	1.2	1.4	1.5	
Stearic acid	0.6	1.2	1.3	1.4	
Myristic acid	0.6	1.1	1.2	1.3	
Dimodan	0.6	1.1	1.3	1.4	
Tristearin	0.6	1.3	1.4	1.6	

^aRatio of absorbances at 630 and 520 nm, the wavelength of maximum absorption for amylose and amylopectin, respectively.

amylose that was complexed increased above 20% for 25% amylose starch, 15% for 50% amylose starch, and 10% for 70% amylose starch. These properties were affected only when complexing lipids were present. With tristearin, no change was observed in expansion ratio, percent of water-soluble carbohydrates, or bulk density. This is interesting because tristearin, being a triacylglycerol, may be thought to act as a lubricating lipid. It appears that the lubri-

Fig. 4. Effect of degree of complexing on expansion ratios of extruded starches.

Fig. 5. Effect of degree of complexing on the percentage of water-soluble carbohydrates of extruded starches.

Fig. 6. Effect of degree of complexing on water-solubility index values of extruded starches.

cating effect of lipids was not significant at the 4% lipid substitution level used in this study.

There is an optimum ratio of amylose and amylopectin for maximum expansion of extrusion-cooked starches, indicating that both amylose and amylopectin contribute to expansion of starches (Chinnaswamy and Hanna 1988, 1990). Decreases in expansion and increases in bulk density of extrusion-cooked starches with complexing lipids may be caused by an alteration in the ratio of free amylose to amylopectin. According to Guy and Horne (1988), the elastic character of the molten extrudates creates a die swell that controls the overall expansion of the extrudate. Launay and Lisch (1983) suggested amylose-lipid complex formation was the key factor influencing the flow properties of starch pastes. When starch is extrusion-cooked, expansion is dependent on the formation of a starch matrix that entraps the water vapor, resulting in formation of bubbles (Harper 1981, Guy and Horne 1988). It is reasonable to speculate that addition of lipids might have affected the character of this matrix (i.e., the viscoelastic properties of the molten extrudate) so that it could no longer hold water vapor, resulting in lower expansion and higher bulk densities. However, this needs to be confirmed through rheological studies.

The decrease in expansion and the increase in bulk density of starch can also be compared to the swelling of native starch upon gelatinization. Swelling is generally considered a property of amylopectin. Amylose is considered a diluent. The amylose and native lipids present in cereal starches may inhibit swelling under conditions when amylose-lipid complexes are likely to be formed (Tester and Morrison 1990). According to Krog (1973), complex formation with the linear component of starches makes the structure more rigid and stabilizes the swollen granule against breakdown, resulting in restricted swelling. That logic is in agreement with our observations.

The decrease in the percentage of water-soluble carbohydrates can be attributed to the insolubilization of the complexed amylose. This also may be due to decreased degradation of amylopectin due to the lubrication effect of lipids. In this study, water-solubility index values were also determined. Water-solubility index is a measure of dextrinization of starch. The percentage of watersoluble carbohydrates of the starches was higher than the watersolubility index values. Similar results were obtained by Mercier and Feillet (1975).

As complexed amylose increased, the water-solubility index values, like the percentage of water-soluble carbohydrates, also decreased. However, the water-absorption index was not affected by addition of lipids.

CONCLUSIONS

The extent of complex formation of starch with lipids depended upon the type of lipid and the amylose content of the starch. X-ray diffraction was used to obtain qualitative evidence of complex formation with lipids. IBC was used to quantify the extent of complexing. There were more complexes formed in starches with higher amylose content. Both IBC and X-ray diffraction indicated that maximum binding occurred with myristic acid and 70% amylose starch. Addition of fatty acids and monoglyceride decreased the expansion ratio, percent of water-soluble carbohydrates, and water-solubility index; increased the bulk density; and did not affect water-absorption index. Except for the waterabsorption index and the water-solubility index, other properties reached limiting values as the amount of complexed amylose increased over 10-20% for starches with 25-70% amylose.

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ENGINEERING AND PROCESSING

Extrusion Processing Conditions for Amylose-Lipid Complexing'

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ABSTRACT Cereal Chem. 71(6):587-593

Normal corn starch containing 25% amylose was extruded with and
without stearic acid and at various combinations of barrel temperatures,
served at 110-140°C barrel temperatures, 140 rpm screw
served, and moisture contents. apparent amylose content (iodine spectra of soluble fraction of extrudates

High-temperature extrusion cooking is used extensively by many food industries to produce various food products with unique texture and flavor characteristics. Desirable properties in the end product are obtained by varying the processing conditions as well as the composition of the raw material. It is recognized that the addition of ingredients such as lipids, proteins, sugar, and salt alter the physical and chemical properties of the extruded foods. Changes in the properties of starchy foods caused by the addition of lipids are attributed to the formation of complexes between amylose and lipids. Researchers have known about the formation of these complexes during traditional cooking processes (like breadmaking) for a long time. Furthermore, complexing has been reported to increase product shelf life. Extrusion cooking of lipid-containing products also results in the formation of these complexes (Mercier et al 1980, Colonna and Mercier 1983, Stute and Konieckey-Janda 1983, Schweizer et al 1986).

Research on extrusion of starches and lipids has been primarily devoted to studying the characteristics of the extrudates. Unfortunately, the manner in which these changes occur has not been as highly researched. Most studies on the effects of processing conditions on lipid binding have been conducted with twin-screw extruders (Mercier et al 1980, Colonna and Mercier 1983, Stute and Konieckey-Janda 1983, Schweizer et al 1986, Galloway et al 1989, Guzman et al 1992). As a result, very little is known about effect of processing variables on complex formation during single-screw extrusion cooking. Twin-screw extrusion studies have been conducted with cereal flours and grits that contain protein, which also binds lipids. Hence, the results reported cannot be applied directly to foods containing varying percentages of starch.

were also evaluated. The addition of stearic acid before extrusion decreased expansion ratio and water solubility index and increased bulk density.

Therefore, the objectives of this study were: to optimize the extrusion processing variables of barrel temperature, screw speed, and moisture content of the feed material for maximum complexing of starch with lipids; and to study the interrelationships and propose the mechanism for complexing that would lead to greater understanding of the effects of extrusion of starches with lipids.

To achieve these goals, the research was divided into two parts.
The first part consisted of single-screw extrusion of normal corn starch with and without the addition of stearic acid. Processing conditions were: temperatures of $110-170$ °C, screw speeds of $110-170$ rpm, and feed moisture contents of $19-25\%$. Comparison was made using a $3\times3\times3$ full-factorial design. The degree of lipid binding was determined using: 1) differential scanning calorimetry, 2) changes in starch iodine-binding capacity (IBC) and apparent amylose content, and 3) wavelength of maximum absorbance for starch.

The second part of the research was a study of the effect of lipid binding on the expansion ratio, bulk density, and water solubility index of the starch-lipid extrudates.

MATERIALS AND METHODS

Materials

Commercially available 25% amylose corn starch was received gratis from American Maize-Products Co. (Hammond, IN). Stearic acid (C18:0) was received gratis from Humko Chemical Division of Witco Corp. (Memphis, TN). A 4% lipid substitution level, based on dry weight of starch, was used for all samples.

To obtain better flow of the material into the extruder, the starch powder was granulated before extrusion. Granulated starch samples were mixed with distilled water in a Hobart mixer (model C-100) to adjust the moisture content to desired levels and were stored in plastic jars overnight before extruding.

Extrusion Process

A laboratory extruder (model 2802, C.W. Brabender, South Hackensack, NJ) with a 1.9-cm barrel diameter and a barrel

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