Spinning of Peanut Protein Fibers[1]

D. L. Fletcher and E. M. Ahmed[2]

ABSTRACT

Raw Altika peanuts were blanched, partially defatted, ground and the protein was removed using an aqueous alkaline extraction, precipitated at pH 4.0 and freeze dried to yield a protein concentrate with 85.5% protein, 3.1% fat and 2.0% ash on a dry weight basis. Peanut protein concentrate was used to produce dope solutions for the spinning of fibers. Viscosity of dope solutions increased rapidly with increases in protein concentration from 11 to 14%; the highest protein concentration gelled within a short time after mixing. Dope solution viscosity increased with increasing NaOH concentration from 0.85% to 0.90%. Higher NaOH concentrations, up to 1.05%, however, resulted in a continued decrease in dope viscosity. Dope viscosity increased as a function of maturation time, especially at NaOH concentrations that yielded the highest viscosities. The best conditions for spinning peanut protein fibers were: 1) dope pH 11.4, 2) maturation time of 12 hours for a 13.0% protein dope or 2 hours for 13.5% protein dope, 3) coagulating bath conditions of 2N acetic acid and 20% NaCl, and 4) dope extrusion pressure of 15 psi. Suitability of dope solutions for spinning depended on the interaction between protein concentration, pH and dope maturity.

Keywords: Peanut protein, peanut spun-fibers, protein fibers, groundnut, protein extraction, dope viscosity.

Peanuts are recognized around the world as a major oilseed crop, grown primarily for their high oil content. Recently, considerable attention has been focused on the peanut, as well as other oilseeds, as a good source of protein to help ease the protein shortage in many areas of the world. Because of harsh and often crude oil extraction techniques, most of this protein is made unfit for human consumption and is often used for animal feed or as a fertilizer (10,12).

The wet-spinning process has been used successfully to produce both textile fibers and edible fibers from vegetable protein sources (2, 13). Peanut protein has been successfully used to produce textile fibers in England (13), but the production of edible fibers for food texturization has been almost solely from soybean protein.

Rhee *et al.* (11) reported on an aqueous system for the recovery of protein and oil from raw peanuts. This procedure utilizes differential pH control and centrifugation to solubilize the protein, separate the resulting fraction and precipitate the protein. The properties of protein solutions (dope) and the variables that affect their behavior have been extensively investigated. Huang and Rha (6) stated that dope viscosity is among the most important physical parameters to be considered in the spinning process. Since the chain lengths of the macromolecules in solutions influence their viscosities, it is reasonable to assume that the dope viscosity could be related to fiber formations. Investigators have found that dope viscosity increases markedly with an increase in protein concentration (3, 4, 5, 6). Circle *et al.* (4) reported that this viscosity rises exponentially with increases in soy protein concentration. Kelley and Pressey (8) found that soybean protein concentrations of 12.5% or less gave viscosities too low for spinning while concentrations of 14.5% or higher yielded gels which could not be spun. Generally, dope viscosity increased with an increase in pH up to a critical point beyond which the viscosity decreased with an additional increase in pH (3, 4, 5, 8). Investigations have shown that dope viscosity can also be influenced by holding time and/or age of the dope solution. Kelley and Pressey (8) found that at the low NaOH concentration of 0.81%, a 13.5% soybean protein dope had a low viscosity which increased slowly with time.

Most procedures report the use of a simple acid-salt combination for use as the coagulation bath in the spinning process. Boyer (2) used a sulfuric acid sodium chloride-formaldehyde bath for textile fibers, the formaldehyde being used also as a curing agent to completely set the fiber before usage. Naturally, formaldehyde cannot be used for fibers in a food application, nor can any chemical which will not produce a product considered safe for consumption. Young and Lawrie (14) used 11% Na_2SO_4 or 20% NaCl in 1N acetic acid to coagulate fibers from blood plasma proteins. They also reported that variation in the type of salt used in the coagulating solution had no apparent effect on the visual appearance of the fibers.

The purpose of this study was to investigate the possibility of spun fiber production from peanut protein.

Materials and Methods

EXTRACTION OF PROTEIN

Raw shelled peanuts of the Altika cultivar, obtained from the Agronomy Department, University of Florida, Gainesville, were used for all experiments. The peanuts were blanched using high pressure water, dried, ground and the fat partially removed with a hydraulic press at 40 tons pressure. The protein was extracted using an alkaline aqueous process as suggested by Rhee *et al.* (11) with the following modification: (a) 600 g of partially defatted meal was mixed with 3000 ml 50°C distilled water, the pH adjusted to 4.0 with 5N HCl and the solid fraction was allowed to settle out and was recovered, (b) the solid fraction was resuspended with distilled water to a volume of 3.5, 1, pH adjusted to 8.5 with 5N NaOH, the mixture was heated to 57° ± 2°C and stirred for 1 hour, (c) the mixture was centrifuged at 1000g for 1 hour. The top fat layer was removed with suction, the

[1]Florida Agricultural Experiment Stations Journal Series No. 6170. University of Florida, Gainesville, FL 32611.

[2]Former graduate student and Processor of Food Science, respectively, Food Science Department.

middle aqueous protein fraction was decanted through several layers of cheese cloth and the bottom solid fraction was discarded, (d) the protein solution was further purified by adjusting its pH to 4.0 with 5H HCl and allowing the protein precipitate to settle out for several hours at 1°C, (e) the supernatant was removed and the protein precipitate was resolubilized to a volume of 3.5 1 with distilled water and steps 2 through 4 were repeated, and (f) the protein concentrate was washed three times with distilled water (pH 4.0), freeze dried at 60°C, and stored at 25°C until used. Proximate analysis (AOAC, 1970) of the protein concentrate indicated 85.5% protein (N X 5.46), 3.1% fat and 2.0% ash on a dry basis.

SPINNING DOPE PREPARATION

A weighed amount of protein concentrate was mixed with 2N NaOH and distilled water using a non-aerating stirrer Model S-30 (Kraft Apparatus Inc., New York) at speed 6 for 3 minutes. The relative amounts of protein concentrate, NaOH, and distilled water were calculated (w/w) to yield dopes of the described protein concentrate and pH. Dope solutions were centrifuged at 10,000 g for 15 minutes prior to viscosity measurements and spinning to remove any entrapped air bubbles and unsolubilized particles.

VISCOSITY MEASUREMENTS

Brookfield Synchro-Lectric viscometers, Models RVT and LVT, equipped with No. 2 cylindrical spindles were used for viscosity determinations at 25°C and speeds as indicated. The dope was placed in 50 ml centrifuge tubes to insure a constant volume and spacing around the spindle. Viscosity is expressed in terms of relative units as read directly from the dial, noting the speed of the spindle. In viscosity measurements made over a period of time the spindle was cleaned at least once every hour and any "skin" on the surface was removed before readings were taken.

SPINNING APPARATUS

The spinning apparatus (Fig. 1) used was designed primarily for laboratory scale spinning of fibers using cellulose dope solutions. It consisted of a dope reservoir

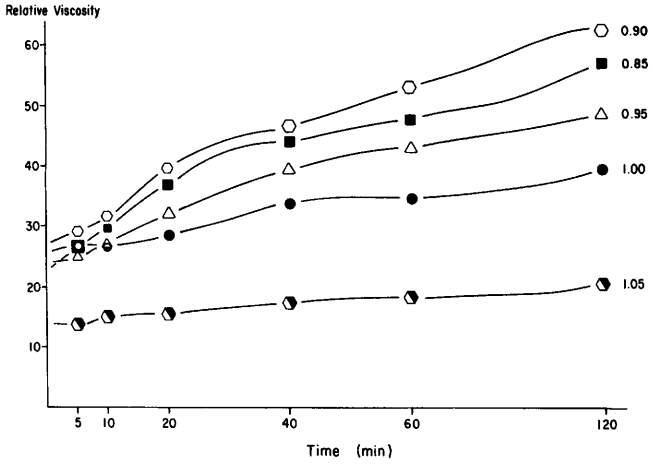

Fig. 1. Spinning apparatus: a) nitrogen tank, b) pressure regulator, c) high pressure line, d) dope reservoir, e) quick open-close valve, f) coagulation bath, g) spinnerette, h) fiber tow, i) tow guide and j) roller assembly.

(d) (capacity 800 ml) connected to a compressed nitrogen tank (a) by a high pressure line (c). A short length of pipe led from the reservoir to a quick open-close valve (e) and to an elbow joint connected to the spinnerette head (g). The spinnerette itself contained 500 holes, each with diameter of 0.064 mm (Englehard Industry).

The coagulation bath (f) was a rectangular trough (capacity of about 8 liters) with a single bar (i) at one end to guide the fibers as they emerge from the spinnerette. A double roller assembly (j) was constructed to collect the fibers and pull them away in such a way as to keep the individual tows separate and distinct. The roller assembly was driven by a variable speed moter run at a speed (29 cm/sec) so as to supply a constant and uniform speed to insure the same tension pulling the fibers away from the spinnerette.

COAGULATION BATH PREPARATION

An acetic acid-NaCl coagulation bath was used in all spinning operations. NaCl was used in amounts of O, 10, 15, 20, and 30 (saturated) percent levels (w/w). Acetic acid was used in ranges of 0, 1, 2, and 3N. The volume of coagulation bath produced for each spinning run was 5 liters. The bath was maintained at 50± 5°C to allow the insertion of hands into the bath in order to manipulate the fibers when needed. The coagulation bath was made fresh for each spinning operation because it was noted early that pH was affected after use, and performance decreased with repeated use.

SPINNING PROCEDURE

About 250 g of prepared and centrifuged dope was placed in the reservoir with care not to entrap any air bubbles in the process. The reservoir top was secured and connected by a high pressure line to a compressed nitrogen tank. The pressure on the dope was regulated to 15 psi and the system checked for leakage.

When the viscosity of the dope reached the spinning range of 70 ± 5 relative units the spinning operation was begun. The viscosity, extrusion pressure, roller speed, and spinnerette to tow guide distance were kept constant for all spinning operations to insure the same degree of stretch for all treatments since it has been shown that degree of stretch can alter the relative strength of the fiber produced (9, 15). While the spinnerette was still out of the bath, the valve was opened and the dope allowed to completely and evenly appear on the outer face of the spinnerette, at which point the spinnerette was lowered into the bath. It is necessary to lower only after the dope emerges, because if the contents of the coagulating bath seeps back into the spinnerette it will coagulate the dope and block passage through the holes.

The coagulated "dope bulb" on the end of the spinnerette was then drawn away by hand, led under the guide, and brought up to the rolled assembly in one continuous motion. The fibers were passed between the rollers, the lower roller brought into contact wiht the upper drive roller and the motor turned on. The turning rollers supplied the needed tension and pulled the fibers at a constant rate away from the spinnerette. The fibers were led away from the rollers by hand to prevent them from clinging to and being wound around the rollers. The spun fibers emerged in bundles or tows of about 500 fibers. At this point the spinnerette was removed to the opposite end of the bath to ensure the maximum resident time of the fibers in the bath.

The resulting tow of fibers was then examined visually and those areas that contain defects due to bulb formation were removed. The lengths of tow were then loosely wound around a smooth wall glass beaker, placed in a 0.05 M phosphate buffer solution (pH 4.0) and held at 1°C until tested.

Results and Discussion

DOPE VISCOSITY INVESTIGATION

Effect of Protein Concentration. Viscosity determinations of freshly prepared aqueous protein showed that viscosity increased rapidly with an increase in protein concentration (Fig. 2). This is a normal characteristic of protein solutions (3, 4, 6). The higher protein concentrations would often form gels within a short time after mixing.

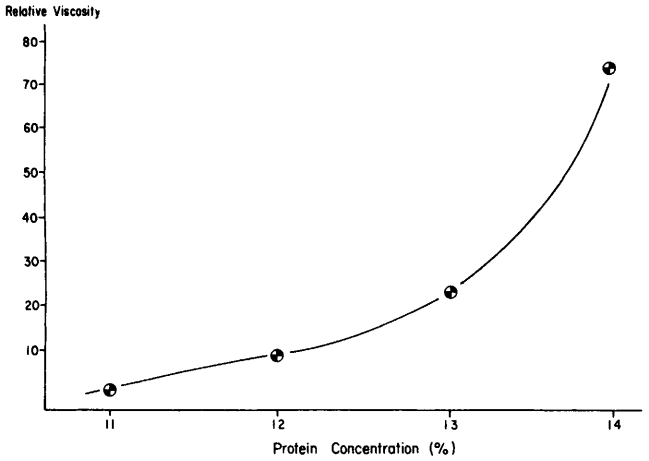

Fig. 2. Dope (ph 10.5) viscosity as a function of protein concentration (Brookfield viscometer model LVF, cylindrical spindle No. 2, 12 rpm, temp. 25°C).

Concentrations above 15% would usually result in gelation during the mixing process while the 15% concentration would usually form a gel shortly after mixing.

Effect of NaOH Concentrations (pH). Dope solutions were produced at a constant protein concentration of 14% and mixed with varying levels of NaOH from 0.85% up to 1.05% increments. The results (Fig. 3) show an increase in dope viscosity

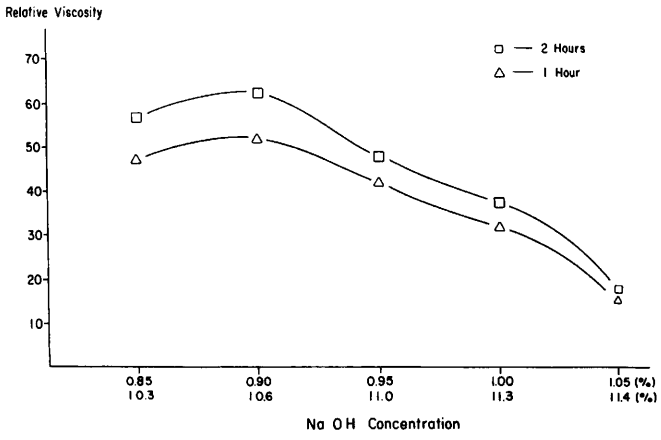

Fig. 3. Dope (14% protein) viscosity as a function of NaOH concentration at one and two hour intervals. (Brookfield viscometer model RVT, cylindrical spindle No. 2, 20 rpm, temp. 25°C).

with an increase in NaOH concentration from 0.85% (pH = 10.3) to 0.90% (pH = 10.6). NaOH concentrations in excess of 0.90% resulted in continual decrease in dope viscosity. Ishino and Okamoto (7) reported similar results with soybean protein and stated that the increase in viscosity is caused by an unfolding and disorientation of the protein molecules. This allows for the formation of new disulfide bonds between the molecular segments that cause the increase in viscosity or gelation. Higher alkaline levels can cause the cleavage of disulfide bonds and the unfolding of protein molecules into smaller units, thus resulting in lower viscosity of protein solutions. High alkaline levels were also shown to cause deammination of some of the amino acids, which can be detected by the odor of ammonia (7). Peanut protein dope solutions with high alkaline levels (1.0 and 1.5%) did exhibit this characteristic of ammonia odors accompanied by decreased viscosities.

Dope solutions below 0.85% NaOH were attempted but all the protein would not go into solution, making viscosity determinations unrealistic. This was probably due to the low alkalinity not being able to cause conformational changes in the molecular structure and leaving the protein molecules in an aggregate formation thus resulting in the low solubility and low viscosity.

Effect of Maturation Time. The effects of maturation time on the resulting viscosities at different NaOH concentrations are shown in Figure 4. Vis-

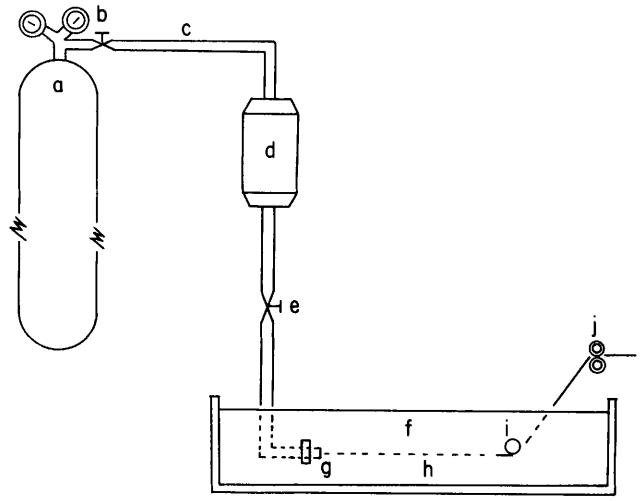

Fig. 4. Dope (14% protein) viscosity as a function of time at various NaOH concentrations (%). (Brookfield viscometer model RVT, cylindrical spindle No. 2, 20 rpm, temp. 25°C).

cosity increased as a function of time. This effect was more pronounced at those NaOH concentrations that yielded the highest viscosities. At the high NaOH concentration of 1.05% there was only a gradual increase in viscosity over two hours whereas the NaOH concentrations of 0.90 and 0.85% showed marked increases. High NaOH levels were found to cause a decrease in viscosity over a several hour period. The effects of maturation time were not determined for long periods of time due to the problem of gelation and "skim" formation of the dope solution. The effect of the decreasing viscosity of the high alkaline dope solutions can be attributed to the cleavage of disulfide bonds and the unfolding of protein molecules into smaller units. The increasing viscosity with time could be attributed to the same basic causes that resulted in the viscosity changes due to alkaline treatment. It is likely that the molecu-

lar unfolding and crossbonding would continue with time until a state of equilibrium between the proteins and the medium is attained. Until that time the viscosity will likely continue to increase in those NaOH concentrations that enhance this effect.

From the results of these investigations it became apparent that dope viscosity was the result of a protein-NaOH interaction on the molecular level and was a function of time. Since viscosity is considered an important factor in dope suitability for the spinning of fibers, these results can be applied to the selection of proper protein-NaOH-maturation time relationships in order to produce dope solutions of the desired viscosity characteristics. It was observed during early investigations that there seemed to be some variation in the results due to differences in the protein concentrate used. A concentrate of lower relative percent protein and higher residual fat level would cause a wider spread in viscosity measurements while dope solutions produced with a more refined concentrate (higher % protein, and less fat) would result in gelation at slightly lower protein concentrations. A similar effect was noted when identical NaOH concentrations in identical percent protein dope solutions would result in a lower pH in dopes produced from a less refined concentrate. This was attributed to the fact that the latter concentrates were more extensively washed to help remove buffering materials. The results reported in this study were obtained from dope solutions prepared from the same extracted batch. The relative differences due to treatment variables therefore remain the same on a qualitative basis. To minimize those fluctuations one large batch was extracted, well mixed, analyzed (1) to insure uniformity and used for the spinning study. This protein concentrate contained 85.5% protein, 3.1% fat and 2.0% ash on a dry weight basis.

FIBER SPINNING INVESTIGATIONS

In preparing dope solutions for spinning, a pH of 10.6 was originally tried in order to yield the highest viscosity, as previously found. This was found to be impractical, however, due to the difficulty countered in trying to adequately solubilize and mix the dope properly. Mixing the dope at a higher NaOH concentrntion (pH = 12.0) and then lowering the pH to 10.6 with 5N HCl was impractical due to the coagulation it induced at contact points of HCl with the dope. For this reason the final spinning dopes were mixed at a NaOH concentration sufficient to give a final pH of 11.4. Such dopes were easily mixed and exhibited the desired viscosity characteristics.

Dope solutions of 13.0 and 13.5% protein were produced at pH 11.4 and spun under identical spinning conditions. The only difference other than protein concentration was that the 13% dope required from 10-12 hours to reach spinning viscosity while the 13.5% dope required only 1-2 hours. Optimum spinning viscosity was 70 ± 5 dial units on the Brookfield viscometer Model RVT equipped with a No. 2 cylindrical spindle, speed 50 rpm, and temp. 25°C. Table 1 lists the abilities of different combinations of NaCl and acetic acid concentrations to induce fiber formation from protein dope solutions (13.0 protein, pH 11.4). The ability of a particular bath combination to induce fiber formation was judged as its ability to produce a fiber tow of sufficient strength to be drawn away by the rollers. The first four bath combinations (Table 1) were found to be inadequate for inducing fiber formation. The dope upon extrusion, into any of these baths, would diffuse out into the bath and precipitate slowly or would produce short segments of fiber tows. The 2N acetic acid: 10% NaCl bath combination was marginal due to its inability to produce fibers on a reproducible basis. Combinations of 2-3N acetic acid: 15-30% NaCl concentrations were capable of inducing fiber formation.

Table 1. Acetic acid-NaCl bath combination and their fiber forming capabilities.

Acetic acid (N)	NaCl (%)	Fiber formation[1]
0	20	-
1	0	-
1	20	-
2	0	-
2	10	±
2	15	+
2	20	+
2	30	+
3	20	+
3	30	+

[1](-) Bath unable to induce fiber formation.

(±) Bath was marginal in ability to induce fiber formation.

(+) Bath adequate to induce fiber formation.

Summary and Conclusions

Protein concentrates extracted from raw blanched Altika peanuts were used to produce protein dope solutions for the spinning of fibers. The effects of protein and NaOH concentrations on dope viscosity, as well as maturation time of the dope were studied. The abilities of different combinations of NaOH and acetic acid concentrations to coagulate the spun fibers were evaluated. Results obtained show that:

1) Dope viscosity increased with protein concentration.

2) Dope viscosity increased with NaOH concen-

tration (0.90%, pH = 10.6) beyond which the viscosity decreased with a continued increase in NaOH concentration.

3) At NaOH concentration less than 1.05%, the viscosity increased as a function of time.

4) Minimum concentration of 2N acetic acid and 15% NaCl in the coagulating bath were found to be required for fiber formation.

5) Optimum dope viscosity for fiber formation was 70 ± 5 dial units using Brookfield viscometer Model RVT with a No. 2 LV cylindrical spindle and a speed of 50 rpm, temp. 25°C.

6) Best conditions for the spinning of peanut protein fibers were 13.0% protein concentration, pH 11.4, maturation time 10 hours at 1°C, coagulating bath conditions of 2N acetic acid: 20% NaCl and dope extrusion pressure of 15 psi.

Literature Cited

1. AOAC. 1970. "Official Methods of Analysis," 11th ed. Association of Agricultural Chemists, Washington, D. C.
2. BOYER, R. A. 1954. U. S. Patent 2,682,466.
3. BURNETT, R. S., E. J. ROBERTS AND E. D. PARKER. 1945. Viscosity patterns of peanut protein solutions: Comparison with other vegetable proteins and with casein. Ind. Eng. Chem. 37:276-281.
4. CIRCLE, S. J., E. W. MEYER AND R. W. WHITNEY. 1964. Rheology of soy protein dispersions. Effect of heat and other factors on gelation. Cereal Chem. 41:157-172.
5. FLEMING, S. E., F. W. SOSULSKI, A. KILARA AND E. S. HUMBERT. 1974. Viscosity and water absorption characteristics of slurries of sunflower and soybean flours, concentrates and isolates. J. Food Sci. 39:188-191.
6. HUANG, F. AND C. K. RHA. 1971. Rheological properties of single cell protein concentrate: Dope formation and its flow behavior. J. Food Sci. 36:1131-1134.
7. ISHINO, K. AND S. OKAMOTO. 1975. Molecular interaction in alkali denatured soybean proteins. Cereal Chem. 52:9-21.
8. KELLEY J. J. AND R. PRESSEY. 1966. Studies with soybean protein and fiber formation. Cereal Chem. 43:195-206.
9. NOYES, R. 1969. "Protein Food Supplements." Noyes Development Corp., Park Ridge, N. J.
10. PARPIA, H. A. B. AND N. SUBRAMANIAN. 1966. Plant protein foods in India. In "World Protein Resources." ed. R. F. Gould, American Chemical Society, Washington, D. C. p. 112.
11. RHEE, K. C., C. M. CATER AND K. F. MATTIL. 1972. Simultaneous recovery of protein and oil from raw peanuts in an aqueous system. J. Food Sci. 37:90-93.
12. ROSEN, G. D. 1958. Groundnuts (peanuts) and groundnut meal. In "Processed Plant Protein Foodstuffs," ed. A. M. Altschul, Academci Press Inc., New York, New York p. 419.
13. TRAILL, D. 1945. Vegetable proteins and synthetic fibers. Chem. and Ind. 8:58-63.
14. YOUNG, R. H. AND R. A. LAWRIE. 1974. Utilization of edible protein from meat industry by-products and waste. II. The spinning of blood plasma proteins. J. Food Technol. 9:171-177.
15. ZIEMBA, J. V. 1969. Simulated meats . . . how they're made. Food Eng. 41:72-75.