ELSEVIER

Carbohydrate Polymers 39 (1999) 37–42

Carbohydrate Polymers

Starch–alcohol complexes

Elzbieta Polaczek[a], Franciszek Starzyk[b], Piotr Tomasik[a,*]

[a]*Department of Chemistry, University of Agriculture, Cracow, Poland*
[b]*Institute of Physics, Cracow Technical University, Cracow, Poland*

Received 9 July 1998; received in revised form 5 October 1998; accepted 12 October 1998

Abstract

Properties of starch complexes prepared from potato starch with methanol, 1-propanol and 1-pentanol are presented. These complexes were prepared from air-and oven-dried starch. It is demonstrated that alcohols penetrated the interiors of starch granules and expelled the amorphous content of the granules through the hilum. In this manner, original structure of granules is irreversibly changed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Starch complexes; Potato starch; Amylopectin

1. Introduction

Starch forms complexes with many organic compounds (Tomasik and Schilling, 1998). Among them are also alcohols. Comparative studies on the complexing ability of amylose and amylopectin provided evidence that only amylose is capable of the formation of helical inclusion complexes, in which alcohols would be guest molecules of the helix cavity (Hollo et al., 1960; Kuge and Takeo, 1967; Jane and Robyt, 1984; Klimek et al., 1991). As a consequence, the size of guest alcohol might be an essential factor for the complex formation and its stability (Kuge and Takeo, 1967). Because contrary to amylose, amylopectin does not complex alcohols, both starch components could be separated either with 1-butanol (Solms et al., 1973; Schoch, 1942,Katzbeck and Kerr, 1950; Kerr et al., 1942; Kerr and Severson, 1943;Cowie and Greenwood, 1957), 1-pentanol (Schoch, 1953; French et al., 1963), cyclohexanol (Meyer and Rathgeb, 1948), isobutanol or isopropanol (Weigel, 1943). The structure of the guest alcohol may determine the character of its interaction with starch (Osman-Ismail and Solms, 1973). It was reported (Rebar et al., 1984) that the starch variety has only a minor effect on the complex formation with alcohols. However, other studies suggested that this conclusion should be questioned. Thus, in spite of the irreproducibility of the absorption–desorption isotherms for granular starch–methanol and starch–ethanol systems, physical sorption was assumed as the sole phenomenon involved, and the swelling of the granule was the argument in this discussion (Gupta and Bhatia, 1969. Our recent studies (Baczkowicz and Tomasik, 1989) revealed that the effect of solvents upon the starch granule might be more complex, and the exposure of starch granules to solvents could produce irreversible damage to granules.

In this study we attempted formation of starch complexes with alcohols in order to improve the combustion of starch applied as the binder for coal briquettes.

2. Experimental

2.1. Materials

Starch was delivered by Szczecin Potato Enterprise NOVAMYL S.A. in Nowogard (Poland). Its characteristics followed Polish Standards for potato starch (PN-A-74710). In the air-dried state it contained 14.23% humidity. Oven-dried starch was produced by heating at 130°C for 2 h.

Analytical grade methanol and 1-propanol were manufactured by Polish Chemicals Enterprise POCh Gliwice, and 1-pentanol (pure) was distributed by VO Sojuzchimexport, Moscow (USSR).

2.2. Preparation of complexes

Starch used in preparations was either air-dried or oven dried (2 h at 130°C). Thus, starch (5g) was suspended in

---

* Corresponding author. Tel.: 0048 126338826, fax: 0048 126336245.
E-mail address: rrtomasi@cyf-kr.edu.pl (P. Tomasik)

PII: S0144-8617(98)00137-4

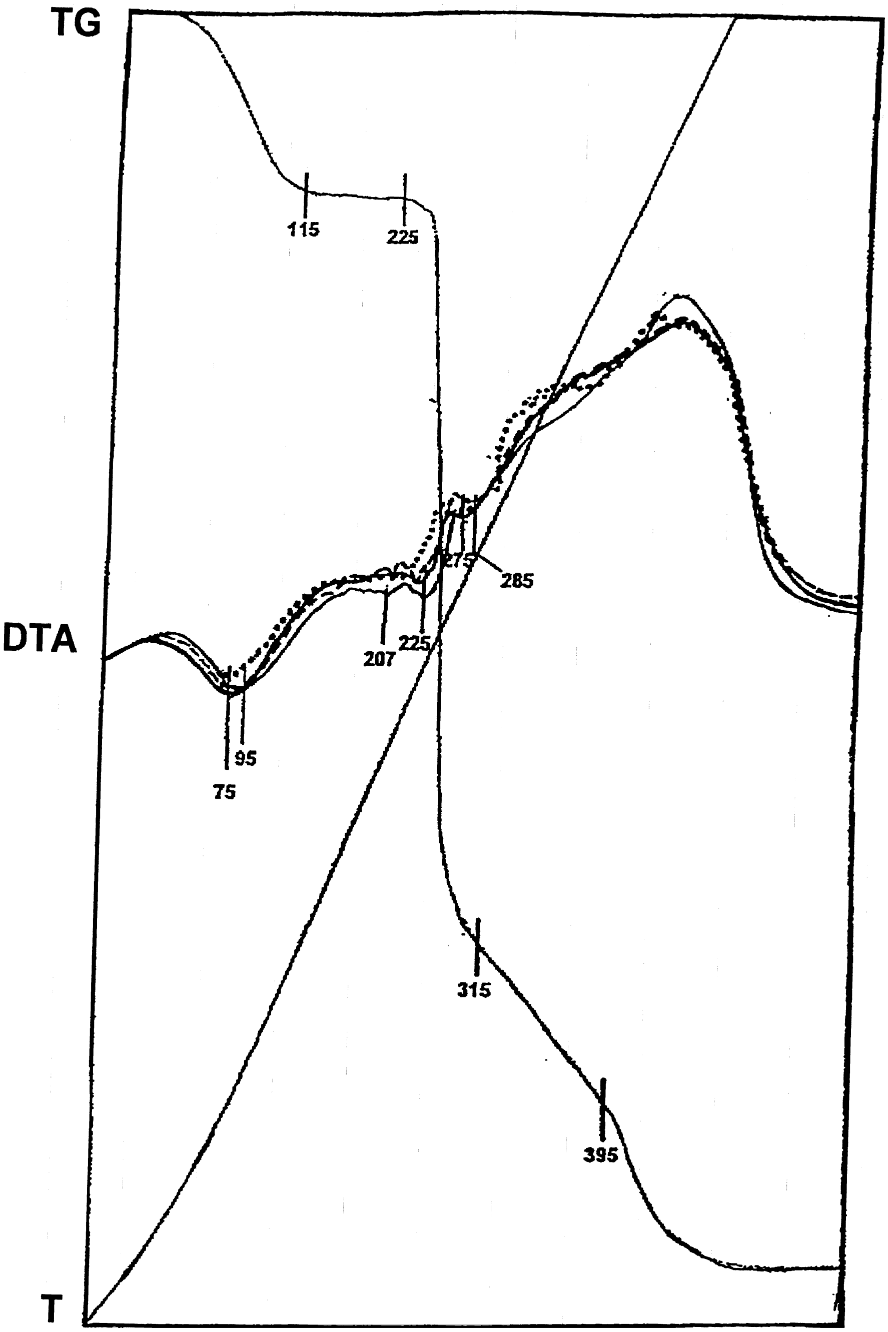

Fig. 1. Thermoanalytical (DTA) curves from the thermograms of plain starch (thin solid line), starch refluxed in methanol (bold solid line), starch refluxed in 1-propanol (dotted line) and starch refluxed in 1-pentanol (pointed line). The thermogravimetric (TG) and temperature increase lines are common for all four starches. Reflux lasted 10 h.

alcohol (25 cm^3) and either agitated at room temperature or refluxed for 24, 48 and 72 h. Starch was subsequently filtered off and left on stand in open air. Dry starch was analysed by thermal gravimetric analysis, WIN-IR spectroscopy, and optical microscopy.

2.3. Thermogravimetric analysis

Starch samples (200 mg) were heated to 450°C in open air with a heating rate of temperature 4°C/min. Corundum ($\Phi = 8$ mm) was taken as the standard. The Paulik-Paulik-Erdey Derivatograph Q-1500 (Hungary) was used for these experiments.

2.4. WIN-IR spectrophotometry

Spectra were recorded using a BIORAD FT-IR 175C spectrophotometer with a diffusive-reflectance accessory

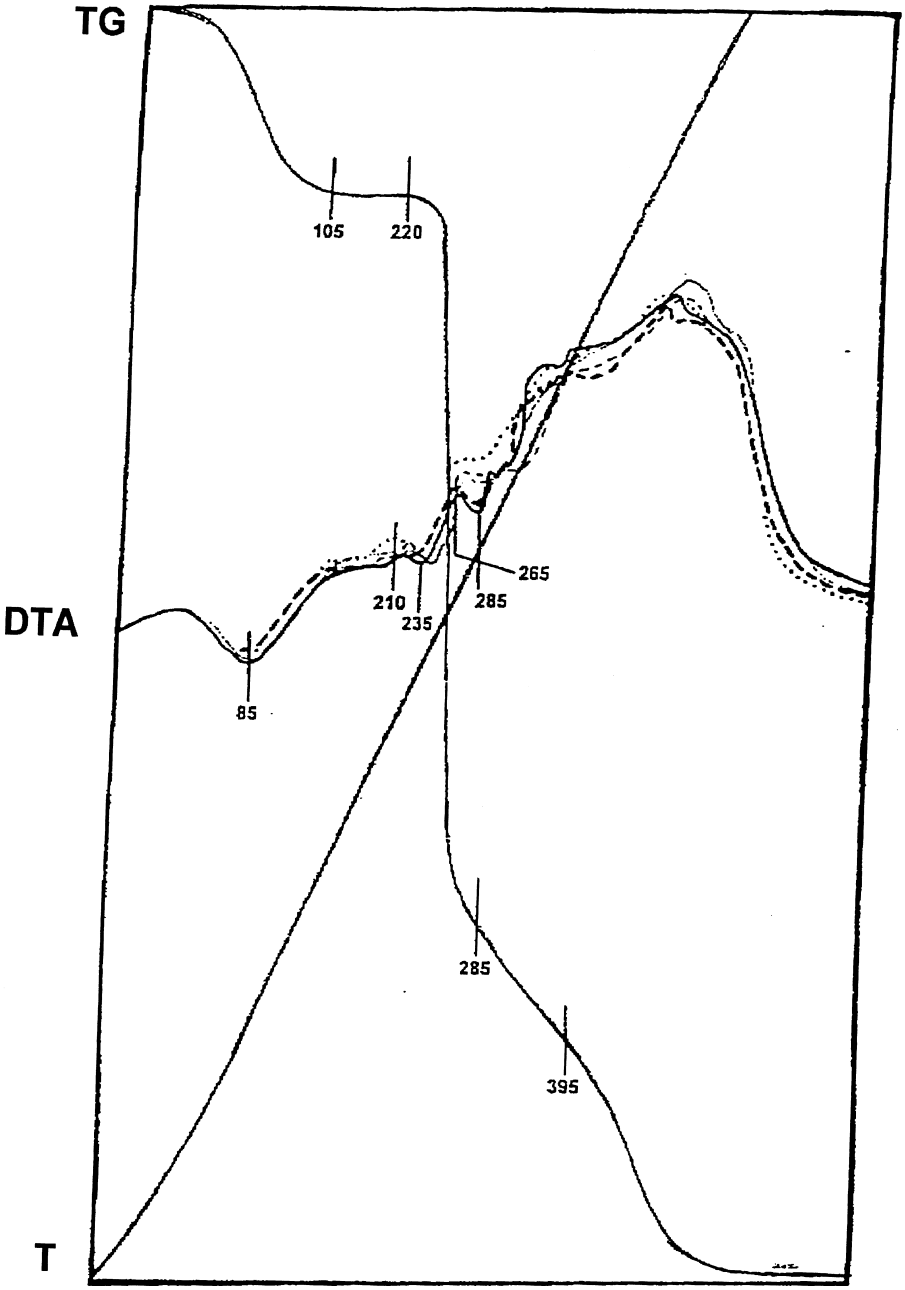

Fig. 2. Thermoanalytical (DTA) curves from the thermograms of starch maintained in 1-pentanol at room temperature for 1 (thin solid line), 2 (dotted line), 3 (pointed line) and 14 days (bold solid line), as well as for starch refluxed in l-pentanol for 10 h (bold dotted line).

manufactured by Pike Technologies Inc. and 1.6 mm sample cups of 4.7 mm in diameter. The band intensities were presented in Kubelka–Munk units f(R) (compensating differences).

2.5. Optical microscopy

Optical observations were carried out using a BIOLAR PI microscope manufactured by PZO Warsaw under 20 × 8 magnification. Photographs were obtained with a MINOLTA camera.

3. Results and discussion

Fig. 1 presents a thermogram of plain, air-dried potato starch together with thermograms of the same starch refluxed for 24 h in methanol, 1-propanol and 1-pentanol. The first weight loss (thermogravimetric curve – TG) had the same course regardless the alcohol used. The accompanying thermal effect on the thermoanalytical curve (DTA) revealed that the weight loss was in all cases attributed to the loss of water. It means that the alcohol complexes not only dried in the open but also decayed, and alcohol was replaced by water.

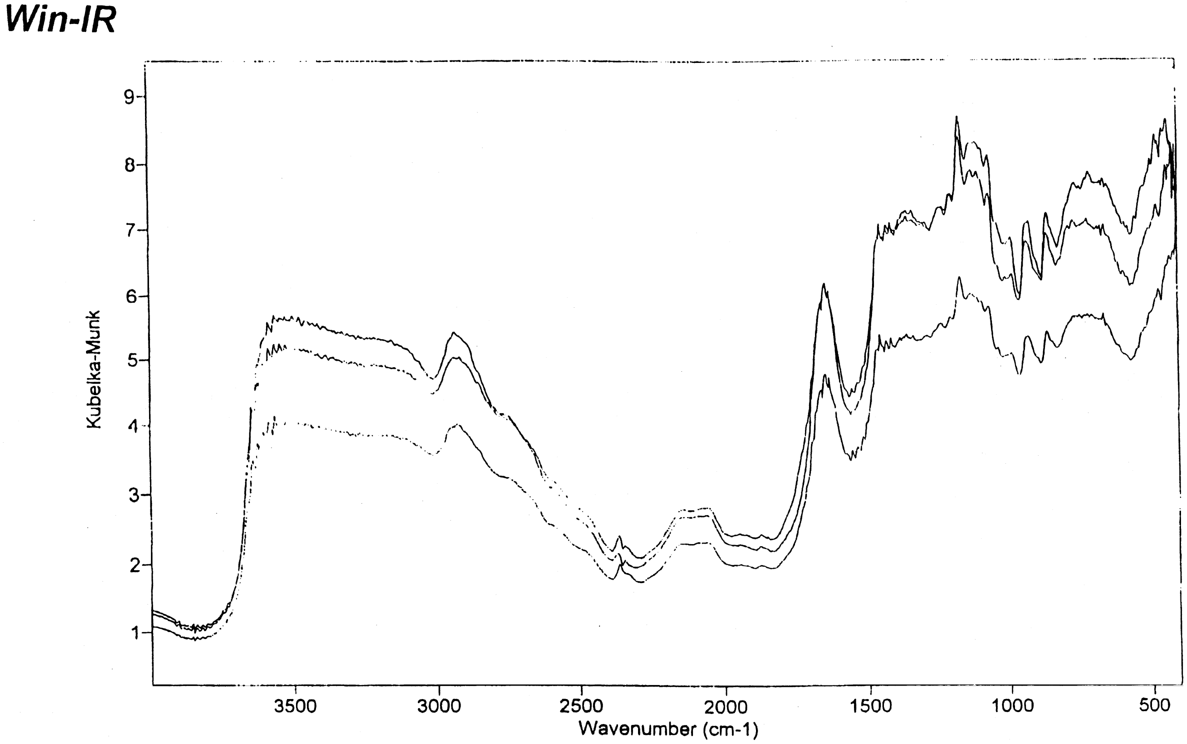

Fig. 3. Win-IR spectra of starch refluxed for 10 h in methanol (top), 1-pentanol (centre) and 1-propanol (bottom).

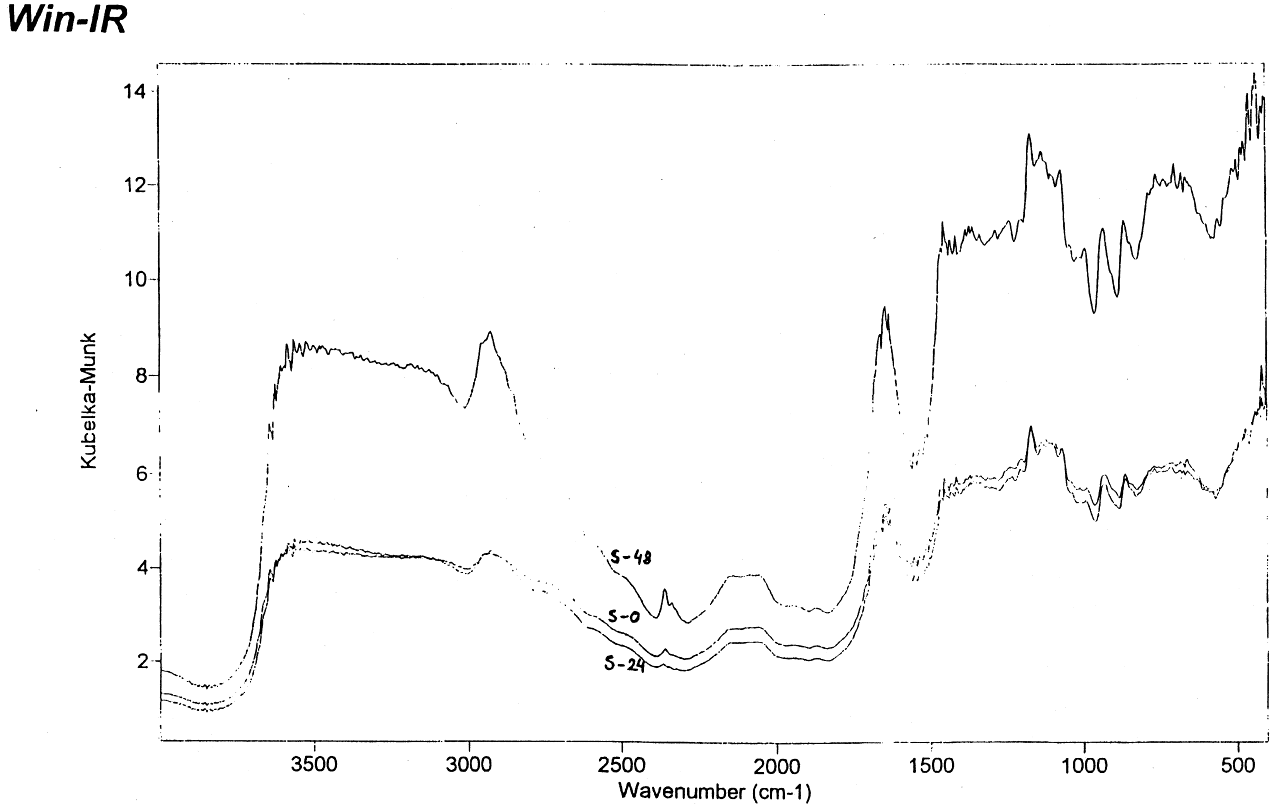

Fig. 4. Win-IR spectra of plain starch (S-0) and starch maintained at room temperature in 1-pentanol for 24 (S-24) and 48 h (S-48).

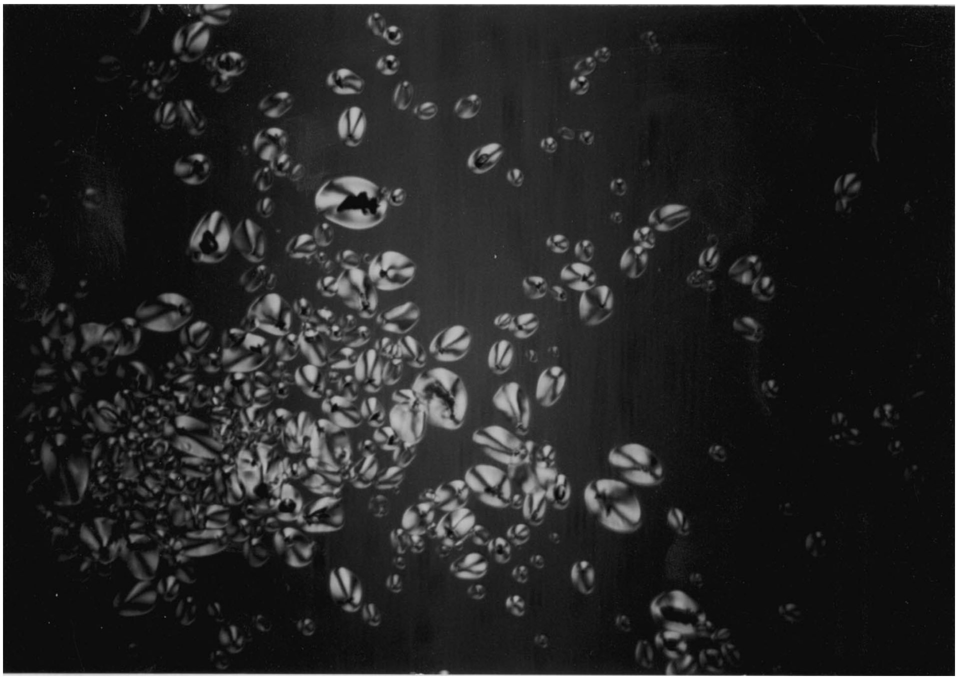

Fig. 5. Granules of potato starch refluxed in 1-pentanol as seen in the polarized light under 20 × 4 magnification. Black areas in hilum are excretions of amorphous content of granules.

The sole difference in the TG curves of plain and alcohol treated starch was observed in the magnitude of the first weight loss of complexes obtained from air- and oven-dried starch. The latter regularly contained 2% less complexed alcohols than the air-dried starch.

It can be rationalized in terms of earlier observations of several repeated water sorption and desorption experiments that the amount of the guest molecules being sorbed decreased with subsequent sorption–desorption cycles (Gupta and Bhatia, 1969). Fig. 1 showed that all differential thermoanalytical curves (DTA) resembled one another. The sole essential difference appeared in the region of 200 to 260°C in which for untreated air-dried starch two thermal effects as small exothermal peaks at 225 and 243°C could be observed. After 24 h of exposure to all of the alcohols tested, even at room temperature, the first peak ceased. Fig. 2 presents the thermograms of potato starch stored in 1, 2, 3 and 14 days in 1-pentanol as compared to the effect of storage in 1-pentanol at its boiling temperature for 10 h.

Two of the most essential differences were associated with the shift of the thermal effect by 8°C to a lower temperature on the DTA curves. Since this effect was ascribed to the loss of included guest molecules this temperature decrease could be interpreted in terms of the mild thermal matrix deterioration in starch. The second difference dealt with vanishing of the exothermic peak at 243°C. Thermograms of starch treated with a given alcohol at room temperature for up to 2 weeks closely resembled those of starch maintained for 10 h in boiling alcohol.

Win-IR spectra in Fig. 3 provide information on the packing density of starch suspended in refluxed alcohols for 10 h. One might see that the band intensities in the spectrum of starch treated with l-propanol are the lowest. Thus, starch treated with this alcohol had the lowest packing density, i.e., the starch granules were least aggregated, and the least number of starch granules occupied the volume of the measurement cup. In terms of the same argument, starch granules treated with boiling methanol packed to the highest density in the measurement cup. Fig. 4 presents such spectra for original starch and for that stored in boiling l-pentanol for 24 and 48 h.

Prolonged heat-alcohol treatment favored starch granule aggregation, and band intensities strongly increased without any band shifts. The non-linearity of the packing density of alcohol treated starch as a function of the position of alcohol in the homologous series may result from the ability of alcohol to form inclusion complexes with amylopectin. Short branches of the latter provided hardly a one- to two-turn helix for the inclusion of guest molecules sufficient to include l-propanol. The hydrophobic chain of methanol was too short to evoke helix formation. l-pentanol could not be included into short helix of amylopectin branches because of its cyclic conformation specific for l-pentanol and 1-hexanol (Pietrzycki et al., 1991).

Inspection of the photograph taken by polarized-light microscopy revealed the reason for the aggregation. This photograph (Fig. 5) demonstrates that alcohol penetrated starch expelling its amorphous content through the hilum. This amorphous excretion caused aggregation.

Results of the study clarify the irreversibility of the solvent action on starch granules and the changes in the appearance of starch granules under the influence of solvents considered as entirely neutral (Baczkowicz and Tomasik, 1989). In another study, (Baczkowicz and Tomasik, 1986) we observed an unusual effect of the azeotropic drying of potato starch with benzene. Gels produced from such starch had essentially different characteristics from gels that were prepared from original starch. The same procedure repeated with corn starch did not affect gel properties with respect to that made of untreated starch (Tomasik and Muzimbaranda, 1993). Thus, the effect of alcohols on starch granules should depend on the starch variety. The inability of starch to hold included alcohols was attributed to the volatility of these guest molecules. N,N'– Dimethyformamide, which was included in starch, could be thermoanalytically recognized after a long duration of storage in open air (Baczkowicz and Tomasik, 1991).

References

Baczkowicz, M., & Tomasik, P. (1986). *Starch/Die Staerke*, *38*, 339.

Baczkowicz, M., & Tomasik, P. (1989). *Starch/Die Staerke*, *41*, 449.

Baczkowicz, M., & Tomasik, P. (1991). *Acta Alimentaria Polonica*, *41*, 269.

Cowie, J. M. G., & Greenwood, C. T. (1957). *Journal of the Chemical Society*, 4640.

French, D., Pulley, A. O., & Whelan, W. J. (1963). *Starch/Die Staerke*, *15*, 349.

Gupta, S. L., & Bhatia, R. K. (1969). *Indian Journal of Chemistry*, *7*, 1231.

Hollo, J., Szejtli, J., Laszlo, E., Gautner, G. S., & Toth, M. (1960). *Starch/Die Staerke*, *12*, 287.

Jane, J., & Robyt, J. F. (1984). *Carbohydrate Research*, *132*, 105.

Katzbeck, W. J., & Ker, R. W. (1950). *Journal of the American Chemical Society*, 3208.

Kerr, R. W., & Severson, G. M. (1943). *Journal of the American Chemical Society*, *65*, 93.

Kerr, R. W., Trubell, O. R., & Severson, G. M. (1942). *Cereal Chemistry*, *19*, 64.

Klimek, D., Poliszko, S., & Pyda, M. (1991). *Acta Alimentaria Polonica*, *17*, 403.

Kuge, T., & Takeo, K. (1967). *Agricultural and Biological Chemistry Tokyo*, *31*, 257.

Meyer, K. H., & Rathgeb, P. (1948). *Helvetica Chimica Acta*, *31*, 1533.

Osman-Ismail, F., & Solms, J. (1972). *Starch/Die Staerke*, *24*, 213.

Pietrzycki, W., Tomasik, P., & Sepiol, J. (1991). *J. Phys. Chem.*, 536.

Rebar, V., Fischbach, E. R., Apostopulos, D., & Kokini, J. L. (1984). *Biotechnol. Bioeng*, *26*, 513.

Schoch, T. J. (1942). *Journal of the American Chemical Society*, *64*, 2957.

Schoch, T. J. (1953). In J. A. Radley (Ed.), (pp. 123). *Starch and Its Derivatives*, 1. London: Chapman-Hall.

Solms, J., Osman-Ismail, F., & Beyler, M (1973). *Canadian Institute of Food Science and Technology Journal*, *6*, A10.

Tomasik, P., Muzimbaranda, C. (1993). unpublished results.

Tomasik, P., Schilling, C.H. (1998). *Advances in Carbohydrate Chemistry and Biochemistry*, *53*, 345.

Weigel, E. (1943). *Kolloid-Zeitschrift*, *102*, 145.