DAVID LEE PHILLIPS, JIE XING, CHAN KONG CHONG, HAROLD CORKE

ANALYTICAL CHARACTERIZATION OF CHEMICALLY MODIFIED STARCHES BY FT-RAMAN SPECTROSCOPY

Abstract

We have recently developed an FT-Raman spectroscopic method for measuring the amount of chemical modification of starch samples from a diverse range of botanical sources and amylose contents. In this paper, we present results and FT-Raman spectroscopic calibration curves that can be used to measure the degree of chemical modification for starches that have been acetylated, succinylated, cationic modified, and maleic acid modified. The FT-Raman methodology we have developed is much faster than currently used wet chemistry techniques, is nondestructive of the sample, needs almost no sample preparation, does not require use of hazardous chemicals, and can be further developed for use as a quality control method for process control in manufacturing.

Introduction

Chemical modification of starches affects their physicochemical properties and their desirability and effective use in manufacturing processes and for particular products [1-4]. It is important to control the amount of chemical modification in order to optimize the starch physicochemical properties for a desired application or product. Usually wet chemistry techniques are still widely used to measure the level of chemical modification in modified starches [5-7]. However, these wet chemistry techniques require time-consuming periods of sample preparation, are destructive of the starch sample, involve chemical hazards and related disposal costs, and are not applicable for use as a quality control method for process control in manufacturing.

We have recently developed applications of Raman spectroscopy to determine the degree of chemical modification in modified starches. In this paper, we present results for the following chemically modified starches: acetylated, succinylated, 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC) cationic modified, and male-

D.L. Phillips, C.K. Chong, Department of Chemistry; Department of Botany; J. Xing, Harold Corke, The University of Hong Kong, Pokfulam Road, Hong Kong.

inated. The different chemical modifications have characteristic Raman marker bands that increase in intensity (relative to the native starch Raman bands) as the amount of chemical modification increases. The characteristic Raman bands associated with the functional group of the chemical modification can be used as a convenient indicator of the degree of chemical modification in modified starches. The ratio of the intensity of the characteristic Raman chemical modification band to the intensity of an internal standard native starch Raman band can be used to prepare a Raman calibration curve for the degree of the chemical modification of the modified starch samples. These calibration curves can then be used to find the amount of chemical modification for unknown starch samples from their Raman spectra. The Raman spectroscopic method for measuring the degree of chemical modification in modified starches allows much faster determinations than currently used wet chemistry techniques, is non-destructive of the starch sample, and is less prone to interference from residual impurities than wet chemistry methods.

Because each chemical compound has a different vibrational spectrum, the different substances contributing to a sample spectrum can be distinguished and this helps to minimize interference from impurities on the Raman spectra of a sample. The intensity of Raman bands depend linearly on the amount of compound present in the sample [8, 9] and Raman spectroscopy has long been used as a quantitative analytical method in the pharmaceutical and polymer industries and has been more recently finding increasing applications in food science and industry [9-28]. The Raman band frequencies and relative intensities can sometimes vary significantly with the structure of the compound and the surrounding molecular environment and this may make it necessary to use different calibration curves for samples with different amylose contents and/or botanical source.

Materials and methods

Parent starch samples were purchased commercially and chemically modified to varying degrees as detailed in references 20, 21, 23-25, 27 and 28 to obtain the acetylated, succinylated, CHPTAC cationic modified and maleinated starch samples used to determine the Raman calibration curves. The degree of substitution of the chemically modified starches were measured using the standard wet chemistry methods as described in detail elswhere [20, 21, 23-25, 27, 28]. The FT-Raman spectra of the dry starch samples were obtained using an FT-Raman spectrometer (Bio-Rad, Cambridge, MA) that employed a backscattering geometry. Typical collection times for the Raman spectra were in the range of 5–10 min per sample with spectral resolution of 4 to 8 cm^{-1}. The ratio of the intensity of the appropriate Raman marker band for the chemical modification to the intensity of the Raman band of the parent starch used as an internal standard was determined from the Raman spectra [20, 21, 23-25, 27, 28]. This

ratio was plotted versus the degree of substitution of the chemical modification found from the wet chemistry methods to derive the Raman calibration curves.

Results and discussion

Figures 1–4 display typical FT-Raman spectra of chemically modified starches with varying levels of modification for acetylated, succinylated, CHPTAC cationic modified and maleinated starches. The Raman marker band for the chemical modification functional group (1732 cm^{-1} Raman band for acetylated starches, 1730 cm^{-1} Raman band for succinylated starches, 761 cm^{-1} Raman band for CHPTAC cationic modified starches and the 1600–1760 cm^{-1} region Raman bands for maleinated starches) typically varies strongly with the degree chemical modification. The ratios of the intensity of the chemical modification Raman marker band to the intensity of the parent starch Raman band chosen to be the internal standard were plotted versus the degree of chemical modification determined from the standard wet chemistry methods to obtain the Raman calibration curve (see plots reported in references 20, 21, 23-25, 27, 28). Least squares linear regression fits to the Raman calibration curves found linear correlation coefficients that had values of r > 0.99 which indicates a very high level of linearity of the Raman marker band intensity with the amount of chemical modification. This excellent linearity indicates that the Raman method calibration curves can be used with confidence to determine the degree of substitution for acetylated, succinylated, CHPTAC cationic modified and maleinated starches [20, 21, 23-25, 27, 28]. Table 1 presents typical results for the linear regression analysis of the Raman calibration curves derived from the FT-Raman spectra shown in Figures 1–4. The Raman calibration

T a b l e 1

Linear Regression Parameters For Plots of The Ratios of the Raman Marker Band Intensities to the Intensity of the Internal Standard Raman Band (y) Versus the Degree of Chemical Modification Determined From the Standard Wet Chemistry Method (x). Note y = m x + b where y is the ratio of the Raman marker band intensity to the intensity of the internal standard Raman band; x = the amount of chemical modification measured using the standard wet chemistry method; m = the slope; and b = the y-intercept. See references 20, 21, 23-25, and 28 for more details of the plots and linear regression parameters.

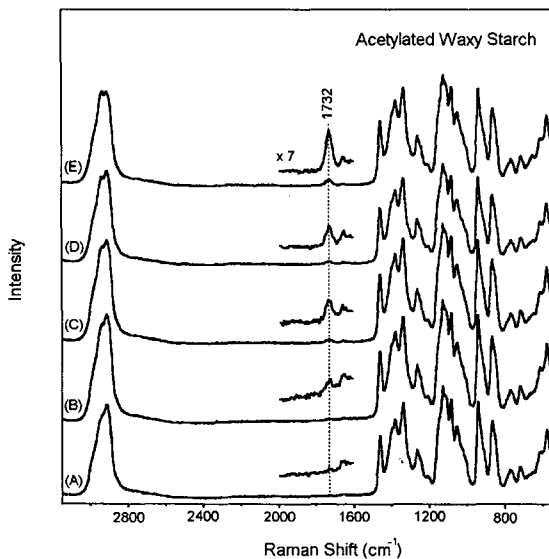| Sample and Modification	Slope (m)	y-intercept (b)	Correlation coefficient (r)
Wheat, Acetylation	0.02277± 0.00114	-0.00162± 0.00225	0.9963
Waxy Maize, Succinylation	0.69427± 0.03182	-0.00183± 0.00144	0.998
Waxy Maize, Cationic	38.81527± 1.135461	+1.8585± 0.0478	0.998
Waxy Maize, Maleinated	6.8741	-0.0006	0.9978

Fig. 1.   FT-Raman spectra of a control non-acetylated wheat starch sample (A) and four acetylated wheat starch samples with differing amounts of acetylation (B-E). Noticeable changes occur in the 1732 cm^{-1} Raman band as the level of acetylation changes. The 1732 cm^{-1} band has been magnified by a factor of 7 so as to more easily observe its intensity changes.
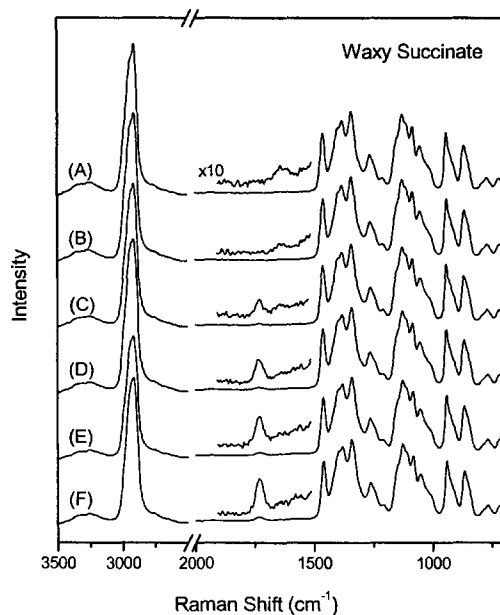

Fig. 2.   FT-Raman spectra of a control non-succinylated waxy maize starch (A) and four succinylated waxy maize starch samples (B-E) with varying degrees of succinylation. The Raman band at 1730 cm^{-1} correlates with the degree of succinylation. The inset of each spectrum shows an expanded view (x 10) of the 1730 cm^{-1} C=O stretch Raman marker band.
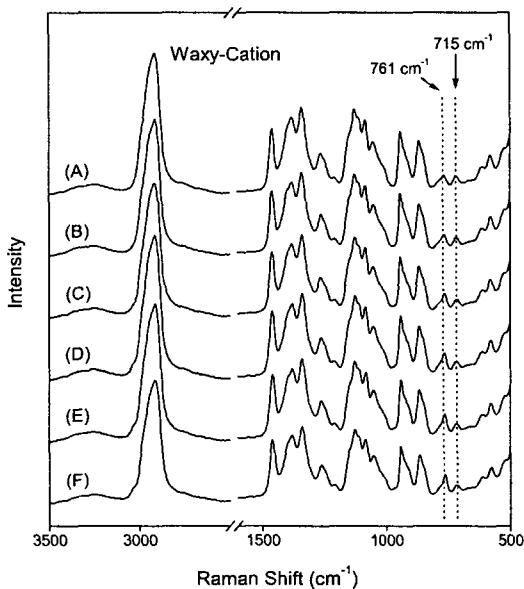
Fig. 3.   FT-Raman spectra of a control non-cationic modified waxy maize starch (A) and five cationic modified waxy maize starch samples (B-F) with different degrees of cationic modification. The Raman band at 761 cm^{-1} increases in intensity as the degree of cationic modification increases.
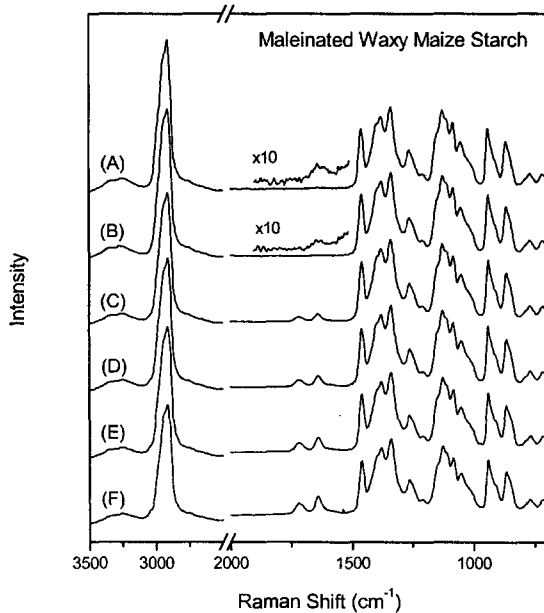

Fig. 4.   FT-Raman spectra of a control non-maleinated modified waxy maize starch (A) and five maleinated modified waxy maize starch samples (B-F) with different amounts of maleate modification. The Raman bands in the 1600 to 1760 cm^{-1} region increases in intensity as the level of maleate modification increases.

curves show some variability due to the amylose content and the botantical source [20, 21, 23-25, 27, 28]. To obtain the best accuracy for the Raman method determination of the degree of chemical modification in modified starches, it is advisable to develop a separate Raman calibration curve for the particular type of starch for which one wants to make routine measurements. The developed Raman calibration curves can be used to obtain the degree of chemical modification for modified starch samples that have un-known levels of modification from their Raman spectra. This Raman technique needs almost no sample preparation, is non-destructive of the sample, is much faster than commonly used wet chemistry methods and is feasible to be further developed for quality control situations in manufacturing processes.

REFERENCES

[1] Mentzer M.J.: Starch: Chemistry and Technology, Academic Press, London, 1984, 543.
[2] Rutenberg M.W., Solarek D.: Starch: Chemistry and Technology, Academic Press, London 1984, 312.
[3] Solarek D.B.: Modified Starches: Properties and Uses, CRC Press, Boca Raton, FL, 1986, 113.
[4] Nachtergaele W.: Starch/Stärke, **41**, 1989, 27.
[5] Genung L.B., Mallat R.C.: Ind. En. Chem. Anal. Ed., **13**, 1941, 369.
[6] Wurzburg O.B.: Methods in Carbohydrate Chemistry IV, Academic Press, New York, 1964, 286.
[7] Kweon M.R., Bhirud P.R., Sosulski F.W.: Starch/Stärke, **48**, 1996, 214.
[8] Long D.A.: Raman Spectroscopy, McGraw-Hill, London, 1977.
[9] Hendra P.J., Jones C.H., Warnes G.M.: Fourier Transform Raman Spectrosopy, Instrumentation and Chemical Applications, Ellis Harwood, Chichester, England, 1991.
[10] Shope T.B., Vickers T.J., Mann C.K.: Appl. Spectrosc., **41**, 1987, 908-912.
[11] Davies M.C., Binns J.S., Melia C.D., Bourgeois D.: Spectrocim. Acta, **46A**, 1990, 277.
[12] Deely C.M., Spragg R.A., Threlfall T.L.: Spectrochim. Acta, 47A, 1991, 1217.
[13] Jackson K.D.O., Loadman M.J.R., Jones C.H., Ellis G.: Spectrochim. Acta, 46A, 1990, 217.
[14] Jones C.H., Wesley I.J.: Spectrochim. Acta, **47A**, 1991, 1293.
[15] Sadeghi-Jorabchi H., Wilson R.H., Belton P.S., Edwards-Webb J.D., Cox D.T.: Spectrochim. Acta, **47A**, 1991, 1449.
[16] Ozaki Y., Cho R., Ikegaya K., Muraishi S., Kawauchi K.: Appl. Spectrosc., 46, 1992, 1503.
[17] Nonaka M., Li-Chan E., Nakai S.: J. Agric. Food Chem., **41**, 1993, 1176.
[18] Li-Chan E.C.Y.: Trends Food Sci. Tech., 7, 1996, 361.
[19] Archibald D.D., Henriksson G., Akin D.E., Barton F.E. II: in Fourier Transform Spectroscopy, AIP, Woodbury, New York, 1998, 653.
[20] Phillips D.L., Pan D., Liu H., Corke H.: Anal. Lett., **31**, 1998, 2105.
[21] Phillips D.L., Liu H., Pan D., Corke H.: Cereal Chem., 1999, **76**, 439.
[22] Phillips D.L., Xing J., Liu H., Pan D., Corke H.: Cereal Chem., 1999, **76**, 821.
[23] Phillips D. L., Xing J., Liu H., Chong C.K., Corke H.: Anal. Lett., **32**, 1999, 2703.
[24] Phillips D.L., Xing J., Liu H., Chong C.K., Corke H.: Anal. Lett., **32**, 1999, 3049.
[25] Phillips D.L., Xing J., Chong C.K., Liu H., Corke H.: J. Agric. Food Chem. in press.
[26] Ma C.Y., Rout M.K., Chan W.-M., Phillips D.L.: J. Agric. Food Chem. in press.

[27] Phillips D.L., Xing J., Chong C.K., Corke H.: Cereal Chem. submitted.
[28] Chong C.K., Xing J., Phillips D.L., Corke H.: J. Agric. Food Chem. submitted.

ANALITYCZNA CHARAKTERYSTYKA CHEMICZNIE ZMODYFIKOWANYCH SKROBI ZA POMOCĄ SPEKTROSKOPII RAMANOWSKIEJ FT

Streszczenie

Opracowano metodę spektroskopową (widma ramanowskiego z transformacją Fouriera) nadającą się do pomiaru stopnia chemicznej modyfikacji próbek skrobi bardzo różniących się pochodzeniem botanicznym oraz zawartością amylozy.

W pracy przedstawiono krzywe kalibracyjne nadające się do tego rodzaju analizy w przypadku skrobi acetylowanych, sukcynylowanych, maleinowanych i kationizowanych.

Opracowana metoda jest o wiele szybsza od obecnie stosowanych, jest nieniszcząca, nie wymaga przygotowania próbek, stosowania toksycznych reagentów i z powodzeniem może zostać rozwinięta jako metoda kontroli jakości w produkcji i reżimu samej produkcji.