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NIR spectra in relation to viscoelastic properties of mixtures of Na-κ-Carrageenan, locust bean gum and casein

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Abstract

Near-infrared spectral data were correlated with the viscoelastic property storage modulus, G′, for mixtures of five biopolymers using multivariate analysis. Gels containing Na-κ-carrageenan (0.5–1.0%) mixed with locust bean gums with two different mannose to galactose ratios, α-casein and/or κ-casein (0–0.5%, polymer concentration) in 0.25 M NaCl were studied. Forty-two experiments based on a multivariate, central composite circumscribed design (CCC) were performed. Partial least square (PLS) regression was used to find a model relation between NIR transmittance spectra, recorded at 15°C in the wavelength interval 400–2500 nm, and the G′ for the biopolymer gels at 15°C. Depending on sample composition, the G′ varies between 0 and 3500 Pa. Cross-validation using a designed data set led to a model based on 11 principal components with a correlation coefficient of 0.85 and a root mean square error of prediction of 540 Pa. © 1998 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Near-infrared (NIR) spectroscopy is an analytical technique with a wide area of application in, for example, the food industry and the pharmaceutical industry (Baughman & Mayes, 1989; Mclure, 1994). NIR spectroscopy in combination with multivariate analysis has been used for composition, classification and quality control of products such as meat, alcoholic beverages, tobacco and tablets (Stark, Luchter, & Margoshes, 1986).

The NIR technique enables overtones and combination bands from fundamental absorption occurring in the IR region of functional groups such as C–H, O–H and N–H to be studied (Baughman & Mayes, 1989). Polymer interactions and compositional and microstructutal properties govern the viscoelastic behaviour of mixed gels. Using Fourier transform infrared spectroscopy (FTIR), it has been shown that conformational and structural changes in κ-carrageenan and retrogradation of waxy maize starch give rise to spectral differences (Wilson, Goodfellow, & Belton, 1988). It was also suggested that FTIR offers a possibility to study gelation and retrogradation in food biopolymers.

Changes in absorption can be observed by studying the NIR spectra with multivariate techniques. Data sets obtained using NIR spectroscopy are suitable for multivariate analysis, since there are many wave-lengths available at which the responses are measured (Howard, 1989). Partial least square regression is a possible method for relating large data sets and calculate model relations (Geladi, & Kowalski, 1986).

In an earlier study, we evaluated the influences of polymer concentration on the viscoelastic properties of a five component biopolymer mixture using multivariate methods (Lundin & Hermansson, 1997). As a complement to this work the possibility to correlate NIR spectral data with viscoelastic properties for a biopolymer mixture was tried in this study. We used partial least square regression to calculate a model relation between NIR spectral data and G′ data for biopolymer gels of κ-carrageenan mixed with locust bean gums, α-casein and/or κ-casein. The results indicate that it is possible to correlate a viscoelastic parameter such as G′ with NIR spectra for these systems.

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2. Material

κ-Carrageenan from Euchema cottonii type III (lot 120H0502), locust bean gum (lot 40H0160), α-casein (lot 82H9575) and κ-casein (lot 104H9538) were purchased from Sigma Chemicals (St. Louis, MO).

The materials used and the experimental design are described in detail in a previous paper (Lundin & Hermansson, 1997). The samples were mixed in accordance with a central composite circumscribed design (CCC). Forty-two samples of polymer mixtures were analysed. The concentration ranges used are 0.5–1.0% for the κ-carrageenan and 0–0.6% for the other polymers. Three experiments are missing from the original full-factorial design, due to instrumental problems with the NIR instrument (Lundin & Hermansson, 1997). These are the mixtures containing:

1. 0.75% Na-κ-carrageenan, 0.6% cold soluble locust bean gum, 0.25% hot soluble locust bean gum, 0.25% α-casein and 0.25% κ-casein;
2. 1.0% Na-κ-carrageenan, 0.5% cold soluble locust bean gum and 0.5% hot soluble locust bean gum;
3. 1.0% Na-κ-carrageenan and 0.5% cold soluble locust bean gum.

3. Methods

3.1. Viscoelastic measurements

The data set from the viscoelastic measurements is the same as in an earlier paper (Lundin & Hermansson, 1997). The small deformation oscillatory measurements were performed in a Bohlin VOR Rheometer (Bohlin Rheology, Lund, Sweden). The measuring system was a serrated coutte-type cup and bob measuring system (DIN 53019). The bob was suspended in an interchangeable torsion bar with a maximum deflection of between 4×10^{-4} Nm and 9×10^{-3} Nm. The strain was kept as low as 4×10^{-4} in order not to disturb the network. This is well within the linear region. The frequency was 1 Hz when the temperature was the independent variable. Samples at 90°C were transferred to the rheometer, which was preheated to 40°C. The sample was equilibrated for 5 min at 40°C. Viscoelastic properties were recorded as the temperature was varied linearly at 1.5°C/min from 40 to 15°C and kept at that temperature for 1 h. After cooling and 35 min storage at 15°C, the data set used in the PLS regression is the G' recorded for 25 min.

3.2. Spectroscopic measurements

An NIR System 6500 spectrophotometer (Perstorp, Sweden) with a spectral operating range of 400–2500 nm and a spectral resolution of 2 nm was used. The spectrophotometer is equipped with Si and PbS detectors.

Using a 2 mm cuvett, transmittance data were determined for the polymer mixtures at 15°C after 1 h storage. Each measurement was preceded and followed by 16 calibration scans against air (1.8 scan/s). The NIR spectrum of each sample (400–2500 nm) was recorded 32 times at 40°C as well as at 15°C.

The hot sample (90°C) was transferred to the cuvett and stored at 15°C for 1 h before NIR measurement. The sample was not thermostatted during the NIR scans.

3.3. Multivariate data analysis

Partial least square regression was used to calculate model relations between NIR data and the storage modulus for the mixed biopolymer system. All statistical calculations were performed using the Unscrambler 6.0 (Camo AS, Norway) software. The number of principal components was established using cross-validation (Wold, 1978). Model performance was defined by the correlation coefficient and the root mean square error of prediction, RMSEP.

4. Results

4.1. Multivariate calibration

NIR spectra for the 39 samples of κ-carrageenan mixed with locust bean gum, α-casein and κ-casein are presented in Fig. 1. Sample data from the whole spectral range, 400–2500 nm, were used as the X-matrix. Applying different spectral enhancing techniques such as multiplicative scatter correction (MSC) or derivatives did not increase the discriminating power of the NIR spectra.

The measured storage modulus for the samples varies between 0 and 3500 Pa. It is noticeable that pure 0.5% Na-κ-carrageenan does not form a gel and 1.0% Na-κ-carrageenan forms a gel with a G' of about 90 Pa. Further, it was observed that addition of the hot soluble locust bean gum led to the strongest gels. All results from the viscoelastic measurements have been presented in a previous paper (Lundin & Hermansson, 1997). The geometric mean of the G' for every sample was taken as response variable (Y-matrix). The geometric mean was obtained by averaging log G' and taking the antilog of the result.

4.2. Partial least square regression (PLS)

PLS regression was performed between NIR spectra and the G' for the samples. The model obtained was cross-validated using all samples. The three-dimensional

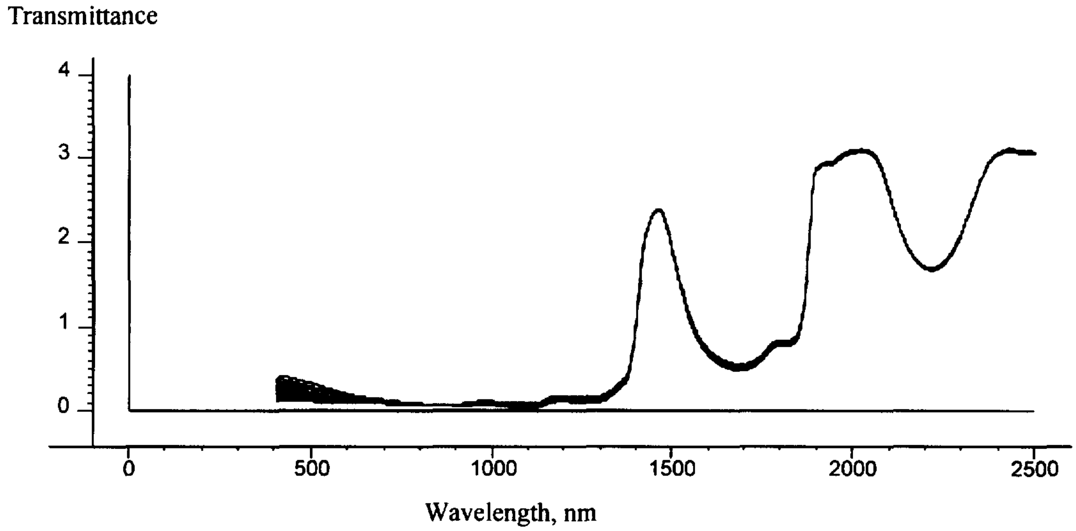

Fig. 1. NIR spectra for 42 samples of Na-κ-carrageenan mixed with locust bean gums, α-casein and/or κ-casein in the 400–2500 nm spectral range.

score plot of the first three principal components from the regression is presented in Fig. 2. The samples are coloured according to their G′. The score plot describes the variation in the samples in both the X-matrix and the Y-matrix. Samples situated close to one another show similar behaviour, whilst samples situated far from each other, along the principal component, have little resemblance. The first three principal components explain 96% of the variation in the NIR spectra and 67% of the variation in the G′ data set. The score plot shows that pc1 mainly resolves the differences in the NIR spectra (92%). Along principal component 2, which resolves 50% of the G′ variation, it is possible to observe an increased storage modulus from left to right.

The mean square error of prediction, RMSEP, for the PLS model of NIR spectra (original and MSC) and G′ is presented in Fig. 3. In the figure RMSEPs obtained after cross-validation as well as leverage correction are presented. For the cross-validated model the best result was obtained using 11 principal components that correspond to an RMSEP of 540 Pa. A model based on MSC spectral data did not increase the performance of the model. Cross-validation of a model based on a designed data set often underestimates the performance of the model, whilst leverage-correction generates a model with an overestimated performance. The RMSEP for a leverage corrected model using nine principal components is 240 Pa.

Fig. 4 shows the PLS prediction of the G′ vs the measured value. Using 11 principal components, a model relation between NIR spectra (X-matrix) and G′ (Y-matrix) was calculated. Model performance showed

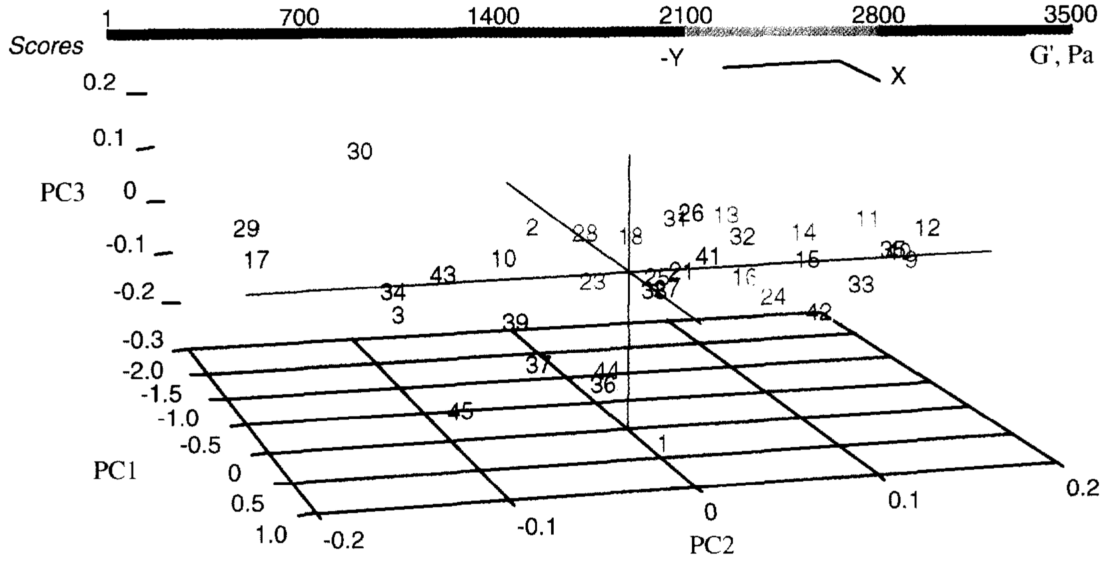

Fig. 2. Score plot of the first three principal components from a PLS regression of NIR spectral data in relation to G′ data. The colours spectrum represent differences in the G′.

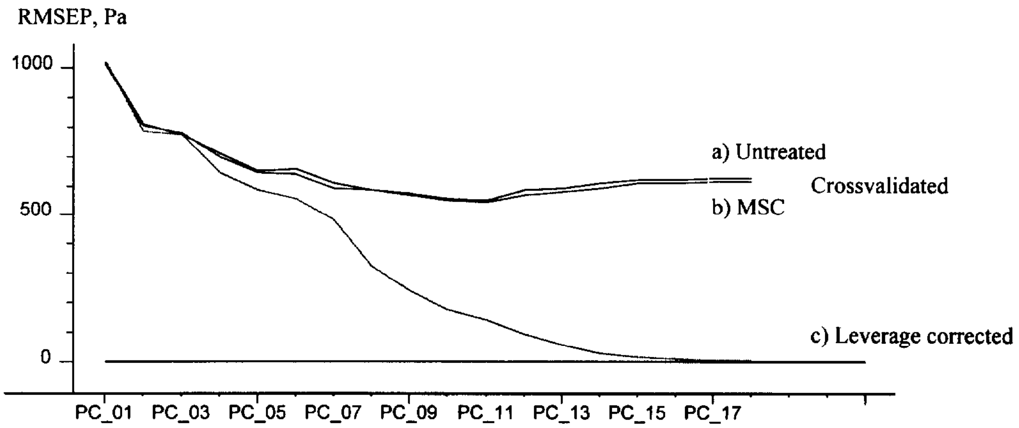

Fig. 3. Root mean square of prediction (RMSEP) as a function of the number of principal components. Cross-validated models: (a) using original NIR spectral data; (b) using MSC NIR spectral data and leverage-corrected model; (c) using original NIR spectral data.

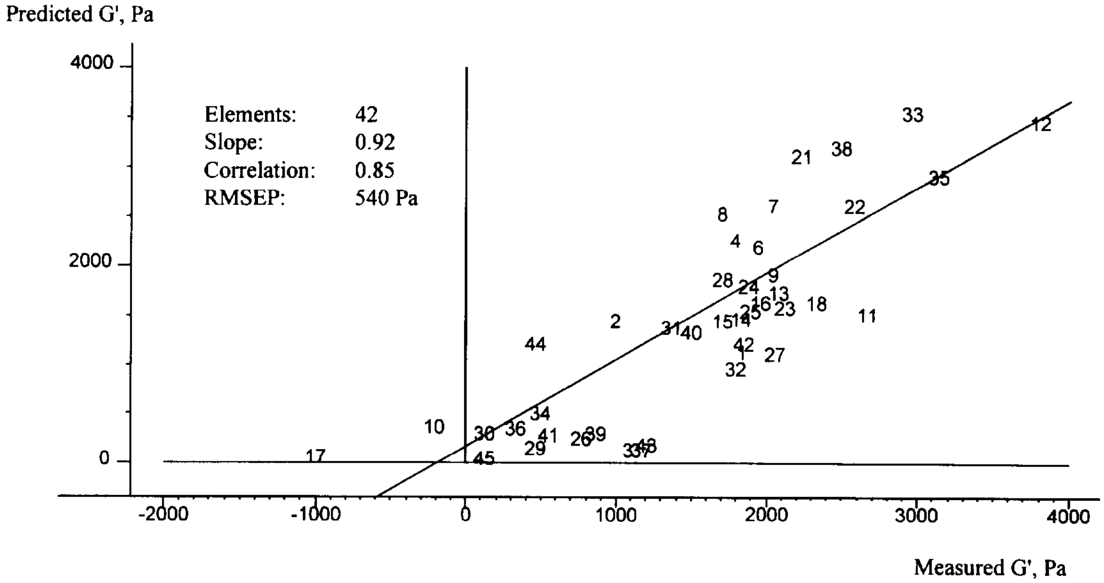

Fig. 4. Measured versus predicted value of G′ from PLS regression. Correlation coefficent 0.85 using 11 cross-validated principal components.

a correlation coefficient of 0.85. The relatively large number of significant principal component necessary to model the relation is probably due to factors giving rise to complex absorption spectra in mixed biopolymer systems such as overtones and combination bands from fundamental absorbance of functional groups and scattering effects due to differences in the microstructure.

To obtain an understanding of which wave-lengths that make a contribution to the calculated model, the average NIR spectrum for the region 400–2500 nm was multiplied by the β-coefficient of the corresponding wave length. This plot is presented in Fig. 5. It can be observed that the wave-lengths contributing the most are in the region 1350–2500 nm. Considering this observation, we performed PLS regression between G′ and NIR spectra using G′ data from this region. The model obtained showed decreased performance compared to the model based on the whole spectra. That is to say that, overall, changes in the whole wavelength interval contribute to the multivariate analysis, but the wavelengths in the region 1350–2500 nm contribute the most.

5. Discussion

The results show that it is possible to correlate NIR spectra and the storage modulus for biopolymer mixtures of Na-κ-carrageenan mixed with locust bean gum, α-casein and κ-casein. Thus, it should be possible to predict the storage modulus by measuring the NIR transmittance spectrum for a mixture of these polymers. An application for NIR spectroscopy could be as quality control or classification of products, although, it would be necessary to have an appropriately calibrated model and a well standardised measuring

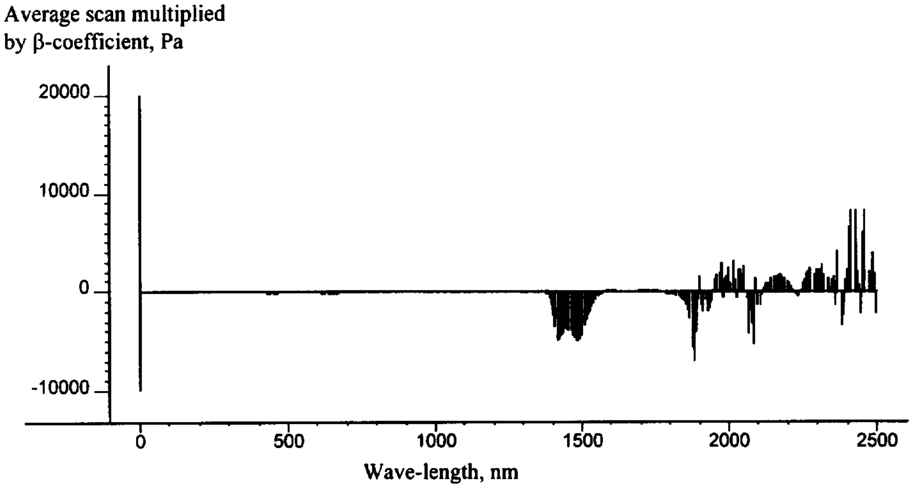

Fig. 5. Average NIR spectrum multiplied by β-coefficient for the spectral range 400–2500 nm.

procedure (Bouveresse, Hartman, Massart, Last, & Prebble, 1996). For the industry, NIR spectroscopy is a quicker and a more cost-effective method than viscoelastic measurements.

The performance of the calculated model shows a correlation of 0.85 and a root mean square error of prediction of 540 Pa, when using 11 cross-validated principal components. The characteristics of the model are obtained using cross-validation. It should also be noted that the G′ vs NIR calibration was performed using 42 experiments from a CCC design. By definition, factorial designs spread the experiments in the experimental domain as much as possible. Therefore using a designed data set when cross-validating the model leads to an underestimated model performance. Thus, the conditions for NIR calibration are not optimal. To improve the predictability of the model and decrease the error of prediction, complementary non-designed experiments have to be performed.

In an earlier study, we showed that the hot soluble fraction of locust bean gum influences the viscoelastic properties of Na-κ-carrageenan more strongly than either the cold soluble locust bean gum, α-casein or κ-casein (Lundin & Hermansson, 1997). The possibility that the hot soluble locust bean gum solely influences viscoelastic behaviour, and consequently, the model relation, was tested. It was found that the locust bean gum concentration can not be solely correlated with either NIR data or G′ data, although the hot soluble locust bean gum influences the mixture strongly.

This study shows that there is a possibility to use multivariate methods to correlate the storage modulus of gels containing Na-κ-carrageenan mixed with locust bean gum, α-casein and/or κ-casein and NIR spectral data with a 0.85 correlation. However, in order to utilise such a relation, as for example for quality control, a more extensive calibration using a non-designed and larger data set has to be performed.

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