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Carbohydrate Polymers 56 (2004) 213–217

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Carbohydrate Polymers

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Geopolymerization of biopolymers: a preliminary inquiry

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Received 27 September 2003; revised 5 February 2004; accepted 7 February 2004

Abstract

The Maillard reaction occurring in biopolymers was investigated to prove that biopolymers could convert to geopolymers over the years. Melanoidin chromophore was used as a marker for the Maillard reaction to take place.

A characteristic property of geopolymers is the high content of humic materials, particularly humic and fulvic acids containing melanoidin. Chitosan can play the role of nitrogen functional groups, forming the precursor of the melanoidin compound. We observed the absorption peak that is identified by UV–Vis Spectrometry, in the chitosan as well as in the glucose–glycine or glucosamine, respectively. This peak represents the formation of melanoidin, the Maillard product. However, xanthan gum, not containing nitrogenous functions, did not yield the melanoidin peak.

The Maillard reactions are dependent upon temperature and reaction time, and occurred in the following experiments: glucosamine, chitosan plus glucose, chitosan plus glucosamine, xanthan gum plus tea, and xanthan gum plus urine. These reactions also depend on the carbohydrate molecules as well as on the existence of nitrogen functional groups. Simple Maillard reaction in biopolymers can help simulate a possible pathway for the geopolymerization phenomena in natural environments.

Keywords: Geopolymerization; Geopolymer; Biopolymer; Maillard reaction; Melanoidin

1. Introduction

Melanoidins are materials formed primarily by the interactions between carbohydrates (carbonyl groups) and amino acids or proteins (free amino groups). The complex network of interactions, resulting in melanoidins as the final reaction products, is commonly referred as the Maillard reaction. It occurs in most foods upon heating or during storage, and also in the human body. The Maillard reaction is responsible for flavor, aromas, nutritional value, textural properties, and color development in food.

The significance of this type of the Maillard reaction is implicit in the formation of melanoidin in a wide variety of natural processes. Organic sediments found in our ecosystem are abound in possible raw materials for the melanoidin reaction, for example, nucleic acids, proteins, polysaccharides, and mucopolysaccharides (Young, Sprang, & Yen, 1974). Therefore, it may also play an important role in the formation of humic acids under natural environments. On the basis of the similarities of the physical and chemical properties of the melanoidins and humic acids (Stevenson, 1982), melanoidins could be precursors of nitrogen-containing humic acids. Humic acids form interpenetrating networks (IPN) with polysaturated triglycerides, which may be a marker for geopolymers.

The concept of geopolymerization has emerged as a possible technological solution for the effective stabilization and immobilization of toxic materials during the last decade (Van Jaarsveld, Van Deventer, & Lorenzen, 1997). It is evident from the literature written by a few scientists that the formation and structure of geopolymers are still poorly understood. Van Jaarsveld and Van Deventer introduced the geopolymers with matrices well suited for the immobilization of toxic materials some years ago. This type of geopolymer, so-called inorganic geopolymer, cannot fully explain the organic containing geopolymers widely existing in the crust of the earth. In this sense, the definition of geopolymers should include both inorganic and organic geopolymers; inorganic geopolymers are the synthetic analogues of natural aluminosilicate materials (Van Jaarsveld, Van Deventer, & Lukey, 2002) and organic geopolymers are the synthetic

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doi:10.1016/j.carbpol.2004.02.006

analogues of naturally occurring macromolecules introduced by Yen. Typical types of inorganic geopolymers can be categorized as kaolinite (clay) and zeolites and organic geopolymers as the bitumen and kerogen, carbonaceous organic macromolecules which have been formed in the lithosphere over the geological time scale.

Characterization of geopolymers in nature can be identified through simulative geo-chamber (pressure cooker) with model compounds and biopolymers. Therefore, simulations should address that biopolymers may covert to geopolymers, although some biopolymers do not contain the nitrogen functional groups. Still, biopolymers can react with soil amino groups, forming geopolymers.

2. Materials and methods

All reactants were dissolved in deionized water and cooked at 105 or 135 °C in an aging chamber, pressure cooker (6 quart) with 15 psi, manufactured by Presto. The conversion time of geopolymers can be shortened by appropriate temperature treatment, as a trade off can be made between time (geological age) and temperature. For this reason, a pressure cooker can be utilized as an aging chamber. Reaction time was applied at 2 or 4 h interval. Glucosamine, glucose, and glycine were prepared for different combinations of experiments, in the concentrations of 0.01, and 0.01, 0.25 and 0.5, 1, 2 M, respectively. Glucose was manufactured by Mallinckrodt and glucosamine and glycine were manufactured by Aldrich. Green tea was used as nitrogen containing organic matter. A tea bag, made by YAMAmotoYAMA, was dipped in the DI water of 250 ml beaker for 20 min. It should be cool for the precipitates to settle down. Human urine was also used. 10 ml of each solution of different concentrations, prepared at a ratio of one to one, was poured into 30 ml vials that would be placed in the chamber with glass wool clogged on top of vials in order to prevent a severe evaporation of solutions. The Maillard reaction in this study was evaluated by UV/visible Spectrometer, Vectra 286/12, Hewlett Packard.

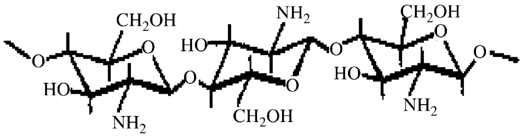
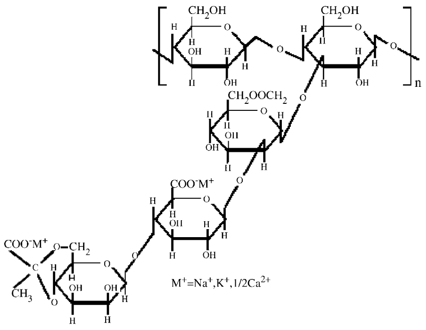
2.1. Biopolymers

Xanthan (0.1 and 0.2%) and chitosan solution (0.1%) were prepared for the Browning effect of the Maillard reaction. Table 1 summarizes the information on biopolymers utilized in this study.

3. Results and discussion

Melanoidin has a strong absorption band between 280 and 300 nm in UV spectra (Young et al., 1974). Measuring the rate of melanoidin formation in model systems will allow early detection of the Maillard reaction. Fig. 1 shows

Table 1
Source, property, and structure of biopolymers (chitosan and xanthan gum)

	Source	Property	Structure	
Chitosan[d] (structural biopolymer)	a derivative of chitin, found in supporting materials of crustaceans (crabs, losters, shrimp, insects, worms, fungi)	• Insoluble material, only soluble in dilute acids • biocompatibility, biodegrability, non-toxicity, polyoxysalt formation, film-forming ability, optical characteristics, adsorption	• 2-acetamido-2-deoxy-β-D-glucose (N-acetylglucosamine) through a β(1→4)-linkage [b] • molecular weight: 1×10^5 to 5×10^5 Daltons. • functional groups: CH_2OH, O, OH, NH_2	
Xanthan gum[e] (extracellular biopolymer)	produced by *Xanthomonas campestris*, a genus of the Pseudomonaceae fa mily	• high viscosity at even low concentration, high viscosity at low shear rates, high degree of pseudoplasticity, high elastic modulus [c] • compatibility with ionic strength variation, heat, pH, shear, enzymes, chemicals	• five sugar residues: two glucose, two mannose, and one glucuronic acid, in the molar ratio 2.8:2.0:2.0 [a] • molecular weight: 2×10^6 to 20×10^6 Daltons (2,000 up to 20,000 repeating units) • functional groups: CH_2OH, OH, O, COOH, H.	

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[a] Garcia-Ochoa et al. (2000); [b] Kumar and Ravi (2000); [c] Kelco brochure (1999); [d] Purchased from MegaCare Inc; [e] CPKelco(Kelzant).

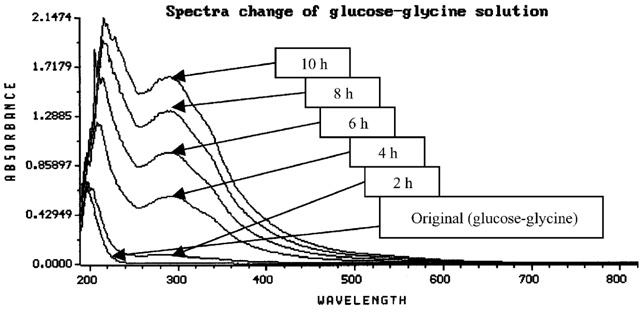

Fig. 1. Melanoidin peaks occurring in the Maillard reaction of model compounds.

the peaks of melanoidin formed in the Maillard reaction of model system (glucose: 0.25 M and glycine: 0.5 M). Melanoidin formation is equivalent to the color change distinctly observed by the naked eyes. This yellow–brown pigment is referred to as a melanoidin chromophore that is simply shown in the crosslinked reaction caused by covalent bonds between glucose and glycine.

Glucosamine (0.01 M) was cooked at 105 °C for 10 h at a two-hour interval. The peaks at 280 nm distinctly grew as the geo-chamber reaction proceeded, shown in Fig. 2. Glucosamine contains the amino group in its structure. No melanoidin peak was shown in the original spectrum of glucosamine. The Maillard reaction occurs under heat when the amino group in glucosamine forms the melanoidins by crosslinking with carbohydrates in the glucosamine. The color became more yellowish as time progressed.

The rate of Maillard reaction is known to be affected by chemical, physical, and physico-chemical factors (Manzocco & Maltini, 1999). Parameters affecting the kinetic behavior of normal Maillard reaction are also true for those of the Maillard reaction occurring in biopolymers, which includes an increase in temperature and time of heating, water activity, pH, carbon-to-nitrogen ratio, the degree of unsaturation, and the chemical aromaticity.

The production of melanoidin varies especially with the temperature and time of heating. Water is produced during the Maillard reaction, thus the reaction occurs less readily with a high water activity, a_w. The concentration of melanoidin produced is very mild. Hence, the product from the Maillard reaction in this study can be a low molecular weight water-soluble Mailllard reaction product (LMW).

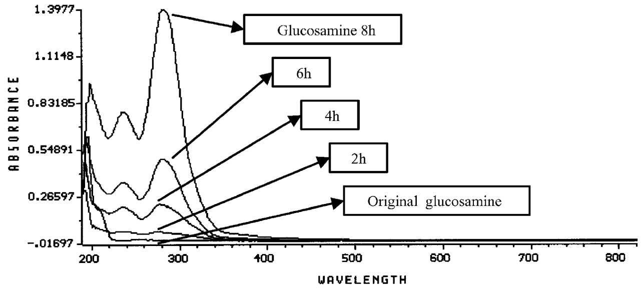

Fig. 2. The Maillard Browning of glucosamine at a different time frame.

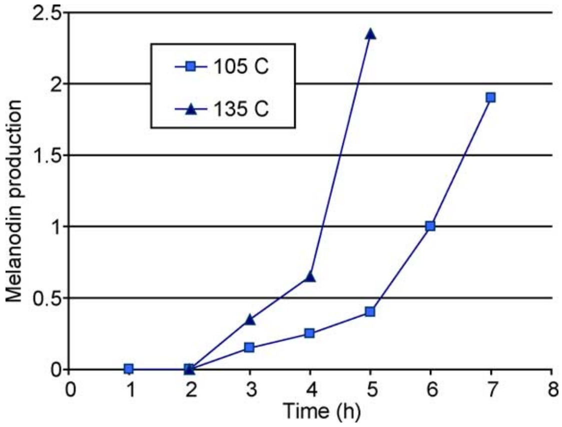

Fig. 3. Melanoidin production at different aging time and temperature.

The Maillard reaction in chitosan solution is totally dependent on aging time and temperature as original chitosan does not have any peak around 280 nm as shown in Fig. 6. In Fig. 3, the production of melanoidin compound increases with temperature and aging time increasing, although many intermediates are involved. It shows the reaction time and temperature dependence in the Maillard reaction of chitosan. The Maillard reaction is also influenced by the participating reactants.

Chitosan + Glucose (0.01 M) was compared with glucosamine (0.01 M) at the same reaction time of 8 h. Original chitosan dose not have middle peaks around 220–260 nm. Both peaks are in the same shape in Fig. 4, which means chitosan + glucose forms glucosamine under heat. Chitosan plays a role in providing nitrogen functional group, thus producing the melanoidin with glucose, carbohydrate. Both peaks have the distinct melanoidin peak.

Chitosan + Glucosamine (0.01 M) was also cooked for 8 h, and compared with glucosamine (0.01 M) and chitosan + glucose (0.01 M). Chitosan + Glucosamine showed the same melanoidin peak in Fig. 5, although it had different shapes of peaks, comparing with those of glucosamine and chitosan + glucose around 200–260 nm.

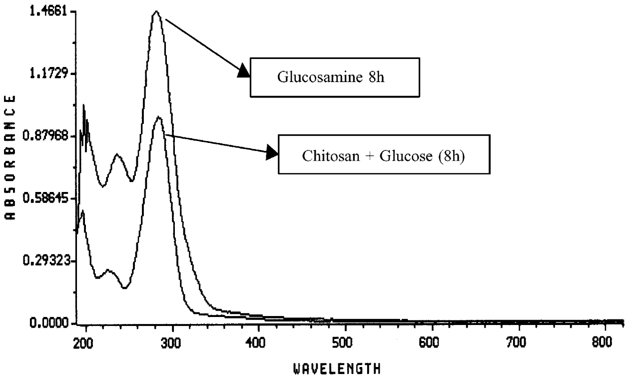

Fig. 4. Spectra comparison of glucosamine and chitosan + glucose in the Maillard Browning.

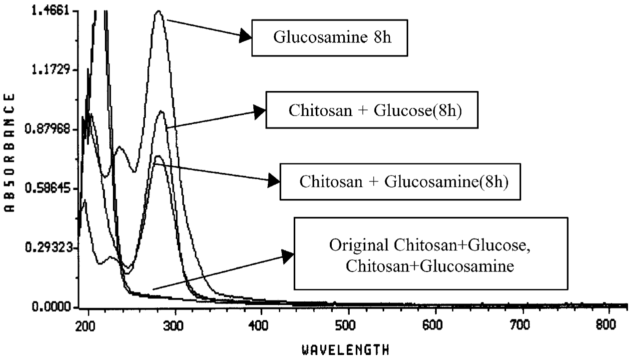

Fig. 5. The Maillard Browning of chitosan + glucose and chitosan + glucosamine.

Taking into consideration the original spectra of chitosan + glucose and chitosan + glucosamine, heat obviously changed the chemical structure of samples. Chitosan + Glucose has higher concentration of melanoidin formation than Chitosan + Glucosamine that was expected to have more melanoidin production due to its additional nitrogen groups. The Maillard reaction depends on the availability of carbohydrate reacting with amine groups, meaning that extra amine group is not necessary for the Maillard reaction to take place. Also, extra carbohydrate is not required for the occurrence of the Maillard reaction, observing that melanoidin peaks are overlapped in the solution of 0.1 and 0.2% xanthan gum reacting with green tea (Fig. 8).

The color change hardly happened in xanthan gum system while the color apparently changed in chitosan system, although the color change in chitosan was not obvious for 10 h. An observable color change was made after 16 h. The Maillard Browning actually occurred according to the spectra in Fig. 6.

Chitosan shows the same melanoidin's peak around 280 nm as shown in model system of glucose and glycine solution as reaction time progresses in an aging chamber, since it structurally contains a nitrogen compound working as an amino group. However, xanthan gum does not show the melanoidin's peak as shown in chitosan and model system (Fig. 7), due to the reason that it does not contain such a nitrogen function as an amino group, which is necessarily required to make the Maillard reaction happen.

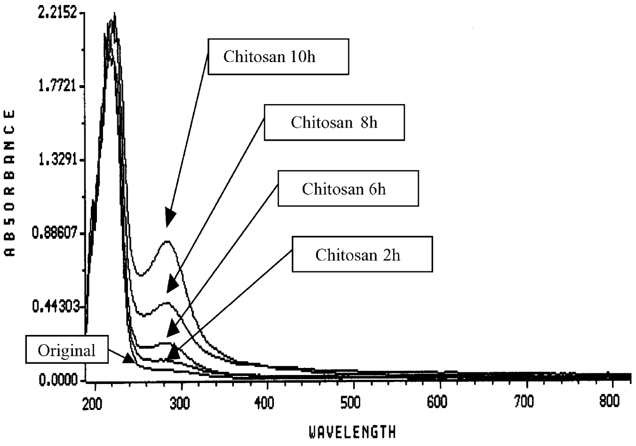

Fig. 6. Spectra of melanoidin in the Maillard Browning of chitosan.

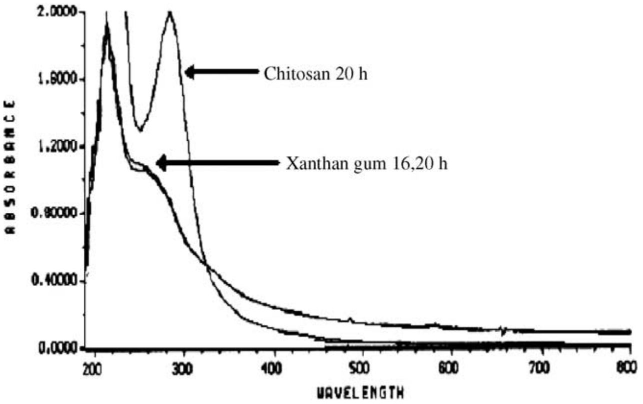

Fig. 7. Comparison of xanthan gum and chitosan spectra in terms of melanoidin.

Biopolymers like xanthan gum, not having nitrogen groups in their structures still have a chance to react with nitrogen containing organic matters occurring in nature, e.g. urine, tea, caffeine, etc. As a result, xanthan gum showed the same melanoidin peak when reacting with such nitrogen containing organic matters, shown in Figs. 8 and 9.

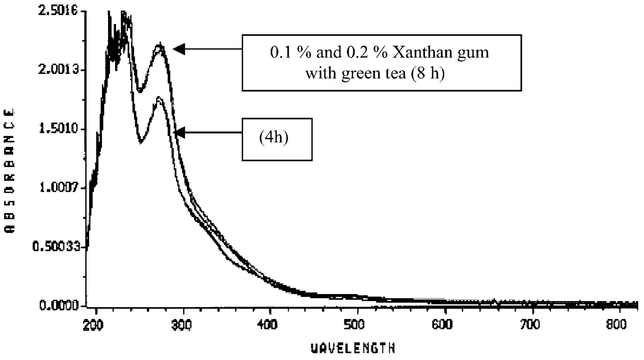

Fig. 8. Occurrence of melanoidin from the Maillard reaction of xanthan gum reacting with green tea.

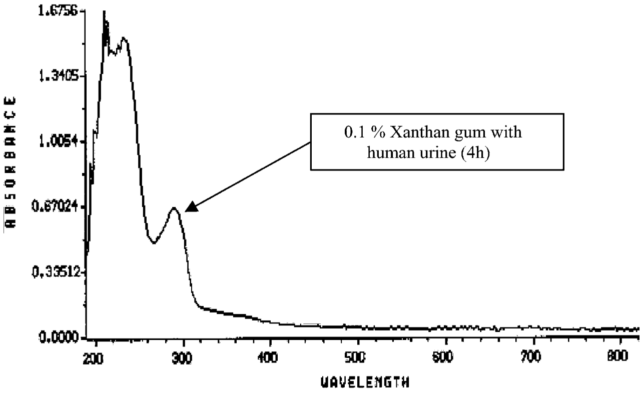

Fig. 9. Occurrence of melanoidin from the Maillard reaction of xanthan gum reacting with human urine.

Theoretically, biopolymers can convert to geopolymers in a natural environment where nitrogen-containing organic compounds are in wide occurrence.

The Maillard reaction can simulate a possible pathway for the formation of geopolymers in nature, a characteristic property of which is the content of high concentration of humic materials, containing melanoidin, a precursor of humic material.

(1) The Maillard reactions occurring in these experiments of glucosamine, chitosan + glucose, and chitosan + glucosamine are strongly dependent upon temperature and aging time. Considering that the original peaks do not have malanoidins, the reactions never take place without temperature.
(2) The Maillard reaction also depends on the carbohydrate molecules as well as on the nitrogen functional groups, which means the appropriate ratio of carbohydrate and nitrogen groups would cause the Maillard reaction to start.
(3) Chitosan can be a source of nitrogen containing organic to make the Maillard reaction happen. It can form melanoidin or humic acid when reacting with a carbohydrate.
(4) Xanthan gum does not show the melanoidin peaks upon being heated unlike chitosan. However, it shows the melanoidin peaks when reacting with nitrogen containing organic materials such as urine, glycine, and green tea, which can take place in natural soil.

Acknowledgements

This work was supported by the US Department of Energy (DOE), under the contract US DOE DE-AC 2601 NT 41307. We would also like to express our thanks to Shivani Yardi for her technical assistance.

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