International Journal of Thermophysics, Vol. 25, No. 2, March 2004 (© 2004)

Determination of the Thermal Diffusivity of Edible Films[1]

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One of the most important factors in the preparation of edible films regards the choice of ingredients. Edible films are commonly prepared with single or mixed high-molecular-weight compounds like proteins and gums. In the present work, protein and gum-based edible films were prepared and their thermal diffusivity determined by photoacoustics. The films were prepared with different concentrations of four basic ingredients: whey protein concentrate, mesquite gum, sodium alginate, and κ-carrageenan. In single-component films, the highest thermal diffusivity was found in mesquite gum ($1.97 \times 10^{-7}\,m^2 \cdot s^{-1}$), followed by sodium alginate, whey protein concentrate, and κ-carrageenan samples. In composed films, the highest thermal diffusivity was obtained in a ternary film made of mesquite gum, whey protein concentrate, and sodium alginate in identical parts ($5.20 \times 10^{-7}\,m^2 \cdot s^{-1}$).

KEY WORDS: edible films; photoacoustics; thermal diffusivity; whey proteins.

1. INTRODUCTION

The development and characterization of edible films have increasingly attracted the attention of biochemists, biotechnologists, and physicists, among others, mainly due to the large variety of applications served by these polymers. Particularly, the capability of edible films to regulate

[1] Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

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0195-928X/04/0300-0611/0 © 2004 Plenum Publishing Corporation

moisture, lipid migration, and gas transport, can be used to improve food quality and extend the shelf life of foodstuff. In addition, edible films play an important role in the covering of thermolabile compounds like vitamins, aroma, and flavors, providing an efficient method to preserve their characteristics during food processing [1].

One of the most important factors in the preparation of edible films regards the choice of ingredients. In the last few years, the use of biomolecules, e.g., proteins, lipids, and polysaccharides, has received special attention. Protein-based films have been prepared with both vegetal and animal proteins, including corn zein, soy protein [2, 3], wheat proteins (glutenin, gliadin) [4–6], peanut protein [7], gelatin, casein [8, 9], and milk whey proteins [10, 11]. On the other hand, edible coatings and films based on polysaccharides have been mainly used for fruit covering due to their excellent selective permeability to O_2 and CO_2. These low-cost films are mostly prepared with derivatives of cellulose, starch, pectins, and gums [12].

A number of studies have also been devoted to the characterization of the mechanical properties [3, 13], and the lipid and flavor permeability of edible films [14]. On the contrary, less attention has been paid to the thermal characterization, in spite of its importance, especially when these films are used for covering thermolabile compounds. In the present work, we determine the thermal diffusivity of composed and single-component polysaccharide-based and protein-based films and correlate it with their microstructure.

2. MATERIALS AND METHODS

2.1. Chemicals

κ-carrageenan (C) was obtained from Germantown (Mexico), sodium alginate (Na-A) from Colloids Naturals de Mexico (Mexico), and whey protein concentrate at 80% protein (WPC) from Ingredientes Funcionales de Mexico (Mexico). Mesquite gum (MG) was collected in San Luis Potosí, Mexico and purified as described by Vernon-Carter et al. [15]. Sorbitol was used as plasticizer (sorbitol: solids content; 0.35:0.65; w:w).

2.2. Sample Preparation

Single-component aqueous dispersions (component:distilled water; 0.025:0.975; w:w) were prepared with a homogenizer (Polytron, Model PT MR 2100) at 25,000 rpm for 90 s. Mixtures of these dispersions were then prepared according to the simplex lattice design [16] (see Table I). For

Table I. Edible Films Prepared with Mesquite Gum, Whey Protein Concentrate (WPC), Sodium Alginate, and κ-Carrageenan

Treatment	Mesquite gum	WPC	Na-Alginate	κ-Carrageenan
1	1.0000	0.0000	0.0000	0.0000
2	0.6650	0.3350	0.0000	0.0000
3	0.6650	0.0000	0.3350	0.0000
4	0.6650	0.0000	0.0000	0.3350
5	0.3350	0.6650	0.0000	0.0000
6	0.3330	0.3330	0.3330	0.0000
7	0.3330	0.3330	0.0000	0.3330
8	0.3350	0.0000	0.6650	0.0000
9	0.3330	0.0000	0.3330	0.3330
10	0.3350	0.0000	0.0000	0.6650
11	0.0000	1.0000	0.0000	0.0000
12	0.0000	0.6650	0.3350	0.0000
13	0.0000	0.6650	0.0000	0.3350
14	0.0000	0.3350	0.6650	0.0000
15	0.0000	0.3330	0.3330	0.3330
16	0.0000	0.3350	0.0000	0.6650
17	0.0000	0.0000	1.0000	0.0000
18	0.0000	0.0000	0.6650	0.3350
19	0.0000	0.0000	0.3350	0.6650
20	0.0000	0.0000	0.0000	1.0000
21	0.2500	0.2500	0.2500	0.2500
22	0.6250	0.1250	0.1250	0.1250
23	0.1250	0.6250	0.1250	0.1250
24	0.1250	0.1250	0.6250	0.1250
25	0.1250	0.1250	0.1250	0.6250

WPC samples, dispersions were heated in a water bath at 90°C for 30 min [17]. The Na-A and C dispersions were heated in water at 60°C. The MG dispersions were heated at 80°C for 30 min to denaturalize their protein fraction [18]. Sorbitol was added as a plasticizer and then vacuum was applied to remove bubbles that could eventually form pinholes during or after film drying. Finally, 20 mL of the dispersions were spread onto rimmed, smooth Teflon casting plates of about 14 cm internal diameter, which were placed on a level surface at room temperature (20°C and $35 \pm 5\%$ RH).

2.3. Photoacoustic Measurements

The thermal diffusivity of edible films was determined by photoacoustics, specifically, we used the open photoacoustic cell (OPC) method. This

method consists of mounting the sample onto the front sound inlet of a cylindrical electret microphone in such a way that a photoacoustic (PA) cell is formed by the sample and the interior walls and membrane of the microphone [19, 20]. A chopped light beam of appropriate wavelength is used to excite the sample. When nonradiative de-excitation processes take place, different mechanisms of heat generation can be observed, e.g., thermal diffusion, thermoelastic bending, and thermal expansion. Depending on the chopper frequency of the light beam, the thickness and thermomechanical properties of the samples, one or more of these mechanisms can contribute to the PA signal [20–22].

2.3.1. Experiment

The experimental setup employed to obtain the thermal diffusivity (α) of the samples consisted of a 100 mW Ar laser whose light beam was mechanically modulated with a chopper. The sample was fixed with vacuum grease upon the inlet of an electret microphone. The microphone output signal was amplified with a lock-in amplifier, and the PA amplitude and phase were measured as a function of the chopper frequency f. The PA signal was generated either by thermal diffusion or the thermoelastic bending effect. We describe below both kinds of mechanisms.

2.3.2. Thermal Diffusion Mechanism

In the thermally thick region, i.e., when the sample thickness (l) is larger than the thermal diffusion length $(\alpha/(\pi f))^{1/2}$, the thermal diffusivity can be obtained by fitting the PA amplitude (S) to the expression [20, 23, 24]:

$$S = (A/f)\exp(-af^{1/2}) \tag{1}$$

Here, A depends on the light beam intensity, room temperature, geometric constants, and thermal parameters. The coefficient a is related to the thermal diffusivity according to $a = l(\pi/\alpha)^{1/2}$.

2.3.3. Thermoelastic Bending Mechanism

In the OPC configuration, the thermoelastic bending mechanism predicts a $1/f$ frequency dependence of the PA amplitude [22]. The ratio of the thermoelastic to the thermal diffusion contributions depends on α and the thermal expansion coefficient (α_t), as well as on geometrical factors. The thermoelastic bending effect dominates at high frequencies because the thermal diffusion contribution is exponentially damped out. In the thermally thick regime, the expression for the phase of the thermoelastic signal is [21]

$$\varphi = \pi/2 + \arctan\{1/(z-1)\} \tag{2}$$

where $z = l(\pi f/\alpha)^{1/2}$, indicating that α can be obtained from the frequency dependence of the PA phase.

2.4. Atomic Force Microscopy (AFM)

An atomic force microscope (Park Scientific Instruments, Model Autoprobe) was used to examine edible films in the contact mode. A sharpened Si_3N_4 cantilever with a spring constant of $0.2\ N \cdot m^{-1}$ and a V-shaped tip 2000 μm long was positioned over the sample, and 20 μm × 20 μm images were obtained under ambient conditions.

3. RESULTS

The thermal diffusivity of the analyzed films is shown in Table II. The highest value, $5.20 \times 10^{-7}\ m^2 \cdot s^{-1}$, corresponded to the film with mesquite gum, whey protein concentrate, and sodium alginate, in identical parts (treatment 6). As evidence of the strong dependence of the films on the constituents and treatment, we refer to another ternary film, namely, sample 15. Composed of whey protein concentrate, sodium alginate, and κ-carrageenan in identical amounts, this polymer blend had a thermal diffusivity of $0.15 \times 10^{-7}\ m^2 \cdot s^{-1}$. For single-component films, the highest thermal diffusivity was obtained in MG films ($1.97 \times 10^{-7}\ m^2 \cdot s^{-1}$) followed by the Na-A, WPC, and C films, with values 1.34×10^{-7}, 0.71×10^{-7}, and $0.40 \times 10^{-7}\ m^2 \cdot s^{-1}$, respectively. These differences can be attributed to the

Table II. Thermal Diffusivity of the Edible Films of Table I

Treatment	Thermal diffusivity ($10^{-7}\ m^2 \cdot s^{-1}$)	Treatment	Thermal diffusivity ($10^{-7}\ m^2 \cdot s^{-1}$)
1	1.97	14	1.10
2	2.76	15	0.15
3	3.39	16	2.36
4	3.60	17	1.34
5	3.30	18	1.04
6	5.20	19	0.75
7	3.80	20	0.40
8	0.33	21	0.27
9	3.07	22	1.99
10	3.32	23	1.68
11	0.71	24	1.92
12	2.85	25	0.72
13	2.85		

type of molecules that constitute the film, as well as to their chemical bonding, which gives place to different types of chain packaging that modify the availability of unoccupied volume in the biopolymer matrix [25]. Consequently, the films show different topographies, as confirmed by AFM images (Fig. 1). The MG film has the smoothest surface (Fig. 1a), with a continuous structure and an rms roughness of 221 Å. The blisters formed in the surface of the Na-A film (Fig. 1b) contribute to a higher roughness, with an rms of 277 Å. The presence of blisters and depressions in the WPC film (Fig. 1c) leads to an rms roughness of 290 Å. The roughest structure corresponds to the C film (Fig. 1c), with numerous blisters of a similar shape and size, and few depressions; the rms roughness of this film is 290 Å.

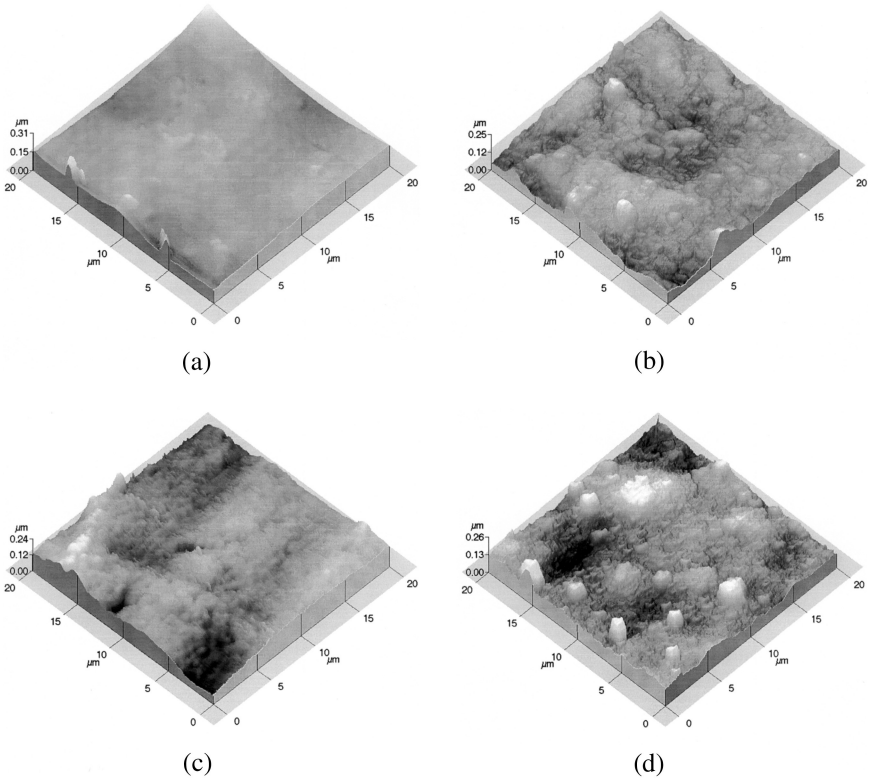

Fig. 1. 20 μm × 20 μm AFM images of biopolymer films: (a) mesquite gum film, (b) sodium alginate film, (c) whey protein concentrate film, and (d) κ-carrageenan film.

Plots of the thermal diffusivity as a function of the constituent concentration, for ternary films, are shown in Fig. 2. The higher thermal diffusivity values occurred in ternary mixtures where the carrageenan (Fig. 2a) or alginate (Fig. 2b) were absent, whereas in mixtures where mesquite gum (Fig. 2c) or whey protein concentrate (Fig. 2d) were not present, the thermal diffusivity was lower. The films with lower thermal diffusivity consisted of binary mixtures of carrageenan and sodium alginate. In this binary film, the thermal diffusivity decreased as the carrageenan content dominated the mixture (see Figs. 2c and 2d). High values of α took place when mesquite gum and carrageenan were present in the film at low proportions of Na-A, due mainly to the MG contribution (see Figs. 2b and 2d). In the case of alginate and carrageenan mixtures, the addition of whey protein concentrate or mesquite gum led to an increment of α values (see Figs. 2c and 2d).

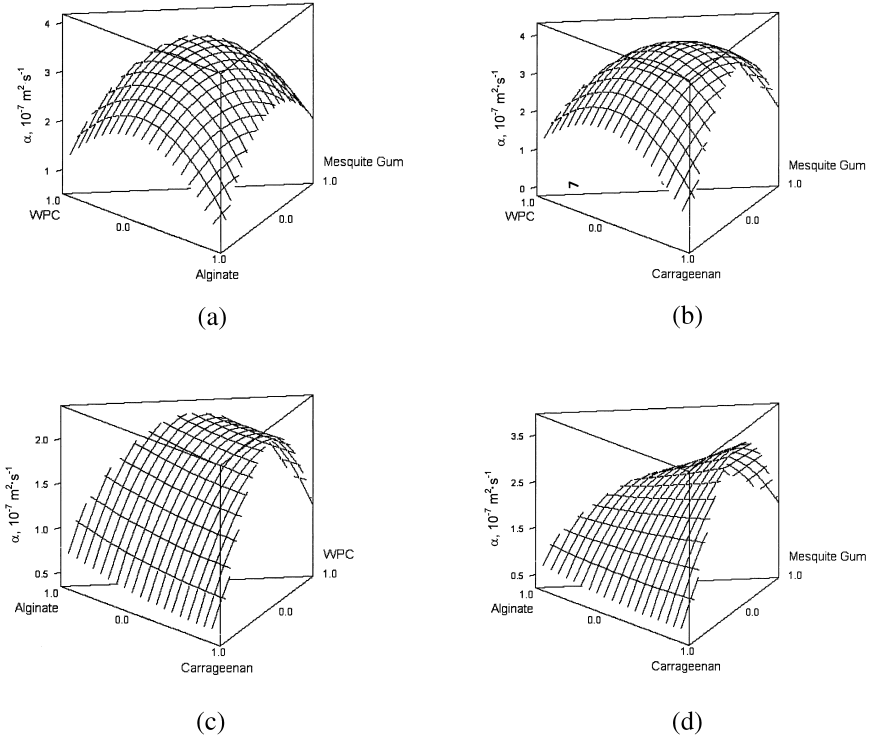

Fig. 2. Surface response of thermal diffusivity for the case of ternary mixtures: (a) without carrageenan, (b) without alginate, (c) without mesquite gum, and (d) without whey protein concentrate.

4. DISCUSSION

The study of interactions between milk whey proteins and polysaccharides has received special attention. The combination of these compounds forms a complex protein-polysaccharide system, whose interactions are different from the individual properties of their components [26]. In the case of sodium alginate-protein films, Veliky [27] has reported that a gel structure of this system is different than the alginate gel alone. This author mentions that the concentration of polysaccharide also has an effect on the system, because a denser membrane is formed when the polysaccharide is increased. Such a membrane assists the polysaccharide-polysaccharide interactions rather than the protein-polysaccharide interactions. The interactions between polysaccharides are expected to enhance the thermal diffusivity of the sample. It is also important to consider electrostatic interactions between both types of molecules [28]. In agreement with Chaparro-Mercado [29], a dispersion of Na-A and WPC has a pH around 5.78, which corresponds to a value slightly higher than the isoelectric point (Ip) of the milk whey proteins. This gives the film a negative charge, similarly to Na-A, favoring electrostatic repulsion and, as a consequence, the formation of aggregates. Under these circumstances, the proteins tend to aggregate and distribute inside the gel. This could explain the decrease of the thermal diffusivity when the Na-A content increases in the WPC binary mixture (Table II).

The carrageenan is also an anionic polysaccharide with sulfate groups and produces aqueous dispersions with pH values around 7 [29]. When carrageenan is mixed with proteins, specifically with WPC, with a pH higher than the Ip of the protein, they can form soluble complexes [30]. When the WPC content prevails over C in this mixture and the pH fulfills the mentioned condition, carrageenan drops are spread in a continuous whey protein gelled network [31]. This continuous network provides higher thermal diffusivity values. On the contrary, when C is present in a higher proportion than WPC, there is no diffusion of C in the milk whey proteins. It increases the aggregation of WPC, producing sites with microseparation of phases in the network [32]. These inhomogeneities in the network certainly tend to decrease the thermal diffusivity.

The MG and WPC interaction occurs at pH values below the Ip of milk whey proteins, because the MG dispersions have a pH value around 4. In these conditions, the proteins are positively charged and the MG has a slightly negative charge [15], which favors the formation of a protein-polysaccharide complex that tends to enhance the thermal diffusivity values as the proportion of WPC is increased in the mixture. For an excess of WPC, α decreases gradually down to the WPC value.

Polysaccharide mixtures produce an increase in the thermal diffusivity (Fig. 2d). In this case, the higher concentration of some components in the mixture also assists the aggregation between molecules of the same component. The mechanism of association could be through hydrogen bonds [33]. Finally, when identical amounts of WPC, Na-A, C, and MG were included in the film (treatment 25), the thermal diffusivity was clearly diminished.

ACKNOWLEDGMENTS

The authors thank E. Ayala and R. Fragoso of the Physics Department, CINVESTAV-IPN for their technical support. This work was partially supported by CONACyT through project 38193-B.

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