

Mechanical and Water Barrier Properties of Biopolyester Films Prepared by Thermo-Compression

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Abstract Four different biopolyester films, two aliphatic polyesters including polylactides (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and two aliphatic-aromatic copolyesters including Ecoplex and Biomax, were prepared using by thermo-compression, and their tensile and water barrier properties were determined. Among the films tested, PLA film was the most transparent (T: 95.8%), strongest, and stiffest (TS, 40.98 MPa; E, 1916 MPa), however it was rather brittle. In contrast, Ecoplex film was translucent while being the most flexible and resilient (EB, 766.8%). Biomax film was semitransparent and was the most brittle film tested (EB, 0.03%). All biopolyester films were water resistant exhibiting very low water solubility (WS) values ranging from 0.03 to 0.36%. PHBV film showed the lowest water vapor permeability (WVP) value (1.26×10^{-11} g·m/m²·sec·Pa) followed by Biomax, PLA, and Ecoplex films, respectively. The water vapor barrier properties of each film were approximately 100 times higher than those of carbohydrate or protein-based films, but about 100 times lower than those of commodity polyolefin films such as low-density polyethylene (LDPE) or polypropylene (PP).

Keywords: biopolymer, biopolyester, film, thermo-compression

Introduction

Bio-based plastic materials derived from renewable resources are considered to be the new generation of packaging materials used in place of non-biodegradable petrochemical-based plastic materials (1-6). Bioplastics have a high potential for specific applications such as packaging (soluble foams for industrial packaging, wrapping film, laminated paper, food containers), fast food tableware (cups, plates, spoons, forks), composting (bags, sacks), agriculture (mulching film, nursery pots, plant labels), and hygiene (diaper back sheet, cotton swabs). Biopolymers can be classified into three broad categories according to their origin: (i) natural biopolymers, such as carbohydrates, proteins, and lipids obtained from plants or animals; (ii) renewable resource-based biopolymers, e.g., aliphatic polyesters, including microbial polyesters such as polyhydroxyalkanoates (PHAs), e.g., polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), and their copolymers, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and chemically synthesized polymers such as poly(glycolic acid) (PGA), poly(ϵ -caprolactone) (PCL), polyvinyl alcohol (PVOH), and polylactides (PLA), as well as (iii) blends or composites of these polymers.

The main factors determining the utilization of these biodegradable plastics are their performance, processing, and cost. Most natural biopolymers have limited use due to problems of performance and processing. On the other hand, aliphatic or aliphatic-aromatic polyesters generally have good performance and processability. Since such polyesters are synthesized by biological means using natural biopolymers, they are usually called biopolyesters (7). Most biopolyesters have high potential for packaging use since they have desirable thermoplastic, biodegradable

and biocompatible properties in addition to high-strength, high-modulus, and good processability.

Like other petrochemical-based plastics, biopolyesters can be processed by various methods such as injection molding, sheet extrusion, blow molding, and thermoforming. Biopolyester films can also be made by various methods such as extrusion, thermo-compression, and solvent casting methods. Extrusion is the preferred method for high throughput production intended for applications such as packaging. The thermo-compression method is also useful as a processing method because of its simplicity and capacity to produce films without solubilization. The solvent casting method has been commonly used for the preparation of biopolymer films (8-10), which involves solubilization, casting, and drying steps. However, the solvent casting method is not suitable for film making with most of biopolyesters, since it involves troublesome steps such as solubilization and drying. In addition, the thermo-compression method is not only a convenient method for testing film properties but is also very similar to processes used presently in the plastics industry (11, 12).

The main objectives of the present study were to prepare biopolymer films using thermo-compression with selected biopolyesters including aliphatic polyesters such as poly(lactide) (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and aliphatic-aromatic copolyesters such as Ecoplex and Biomax, and to characterize the resulting films for their tensile and water vapor barrier properties.

Materials and Methods

Materials Four biopolyesters, PLA (Poly-L-lactate, Biomer[®] L9000), PHBV (13% valerate content), Ecoplex, and Biomax, were obtained from Biomer Inc. (Krailling, Germany), Monsanto Co. (St. Louis, MO, USA), BASF Aktiengesellschaft (Ludwigshafen, Germany), and DuPont Ltd. (Auckland, New Zealand), respectively. Ecoplex and

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Biomax are trade names of aliphatic-aromatic biopolyester produced from BASF and DuPont, respectively. All resins were dried in a vacuum oven at 60°C for 24 hr before use.

Preparation of films Thermo-compressed biopolyester films were prepared using the thermo-compression method described by Rhim *et al.* (11). A Carver Laboratory Press (Hydraulic Unit, Model 3925; Carver Inc., Wabash, IN, USA) was used for thermo-compression of biopolymer resins. The compaction temperatures used for each biopolymer film were 20-30°C higher than the melting point of each resin. For PLA and Biomax, a compaction temperature of 210°C was used, and for Ecoflex and PHBV, 150°C was used with the same compaction pressure. About 2 or 3 g of biopolyester resin (2 g for PLA and 3 g for the others) was placed between 2 stainless steel plates (1 mm thick, 25.4 cm wide, and 25.4 cm long) lined with Teflon cloth and then inserted between the platens of the press heated to the compaction temperature. Since the spreadability of PLA was superior to the other resins, less sample (2 g) was used for the preparation of PLA films. After heating for 30 sec at the compression temperature, a pressure of about 10,000 psi (68.9 MPa) was applied for 2 min followed by the removal of the Teflon cloth liners. The compacted film was easily peeled from the Teflon cloth layers after cooling to room temperature.

Film cutting and conditioning All of the films were cut into 7×7, 2×2, and 2.54×10 cm sized pieces for the measurement of water vapor permeability (WVP), water solubility (WS), and tensile properties [tensile strength (TS), Young's modulus (E), and elongation at break (EB)], respectively. Film thickness was measured using a micrometer (Dial Thickness gauge 7301; Mitutoyo, Japan) with 0.01 mm accuracy. All film samples were then preconditioned in a constant temperature humidity chamber (model FX 1077; Jeiotech Co., Ltd., Korea) set at 25°C and 50% RH for at least 48 hr.

Color and transparency The surface color of films was measured using a colorimeter (CR-300 Minolta Chroma Meter; Minolta Camera Co., Osaka, Japan) to obtain Hunter L, a, b, and total color difference (ΔE) values as described by Rhim *et al.* (13). The transparency of films was determined by measuring the percent transmittance at

660 nm using an UV/Visible spectrometer (Lamda 25; Perkin Elmer Instruments, Norwalk, CT, USA).

Tensile properties Tensile strength (TS), Young's modulus (E) and elongation at break (EB) of each film were evaluated with a Model 5565 Instron Universal Testing Machine (Instron Engineering Corporation, Canton, MA, USA). Initial grip separation was set at 50 mm with a cross-head speed of 50 mm/min.

Water vapor permeability (WVP) WVP ($\text{g}\cdot\text{m}/\text{m}^2\cdot\text{sec}\cdot\text{Pa}$) was calculated as:

$$\text{WVP} = (\text{WVTR}\cdot L) / \Delta p$$

where, WVTR was the measured water vapor transmission rate ($\text{g}/\text{m}^2\cdot\text{sec}$) through the film, L was the mean film thickness (m) and Δp was the partial water vapor pressure difference (Pa) across the two sides of the film. The WVTR was determined gravimetrically using a modified ASTM Method. In calculating WVP, the effect of the resistance of the stagnant air layer between the film undersides and the surface of the water in the cups was corrected (14).

Water solubility (WS) The WS of each film was determined according to the method of Rhim *et al.* (13). WS was expressed as the percentage of dry matter dissolved after 24 hr immersion in water at 25°C.

Statistical analysis Each experiment was repeated, and all measurements of TS, E, EB, WVP, and WS were done in triplicate. Statistics using a completely randomized design were determined using the general linear models (GLM) procedure in the SAS program. The significance of each mean property value was determined ($p < 0.05$) with Duncan's multiple range test.

Results and Discussion

General properties of biopolyesters The general properties of biopolyesters used in the present study were obtained from the literature survey and tabulated in Table 1 relative to those of commodity polymers, such as low-density polyethylene (LDPE) and polyethylene terephthalate (PET),

Table 1. Characteristic properties of biopolyesters and other commodity polymers¹⁾

	PLA	PHBV	Ecoflex	Biomax	LDPE	PET
ρ (g/cm^3)	1.25	1.25	1.25 - 1.27	NA	0.910 - 0.925	1.29 - 1.40
MP ($^{\circ}\text{C}$)	175 - 180	130 - 160	110 - 115	ca. 200	98 - 115	245 - 265
T_g ($^{\circ}\text{C}$)	55 - 60	-4 - -7	-30	NA	-100	73 - 80
TS (MPa)	45 - 60	20 - 40	36	NA	19 - 44	48 - 72
E (GPa)	2.7 - 3.0	1 - 2	0.08	NA	0.3 - 0.5	2.8 - 4.1
EB (%)	6 - 15	8 - 25	820	NA	600	30 - 300
Chemical structure	Aliphatic polyester	Aliphatic copolyester	Aliphatic-aromatic copolyester	Aliphatic-aromatic copolyester	Polyolefin	Polyester

¹⁾Tabulated based on ref. 5, 6, 15. ρ , density; MP, melting point; T_g , glass transition temperature; TS, tensile strength; E, Young's modulus; EB, elongation at break; NA, not available.

for comparison.

PLA, a linear aliphatic polyester, is highly versatile and is derived from renewable resources like corn. It has high strength, high modulus, and good processability with properties of thermo-plasticity, biodegradability, and biocompatibility. PLA can be processed by extrusion, thermoforming, injection, blow-molding, fiber spinning, or stretching. It is printable and heat sealable. PLA can be used for food contact surfaces since it is generally recognized as safe. Its actual and potential applications are found in the crop and food sectors (films, food packaging, soft drinks), and for non-woven materials in hygienic products (16, 17).

PHBV is a copolymer of 3-hydroxybutyrate and 3-hydroxyvalerate produced by microbial fermentation. PHBV is a highly crystalline polymer with melting point and glass transition temperatures similar to polypropylene (PP). Due to their characteristics of biodegradability through nontoxic intermediates and easy processability, PHBV polymers are currently used as substitutes for non-biodegradable polymeric materials in commodity applications (5, 6).

Ecoflex is an aliphatic-aromatic copolyester based on butanediol, adipic acid, and terephthalic acid. Ecoflex has a long chain branched structure. It is a thermoplastic material similar to LDPE but with better mechanical properties. It is extruded to make tear-resistant and flexible films for packaging applications. It is resistant to water and is used to make breathable films because of its moderate water vapor permeability (5, 6).

Biomax, a modified form of PET, is a family of aliphatic-aromatic polyesters obtained from the PET with different aliphatic monomers like dimethylglutarate and diethylene glycol. Biomax can be processed by thermoforming and blow or injection molding on standard equipment. Applications include yard waste bags, disposable eating utensils, agricultural films, plant pots, etc. Its properties, according to DuPont, are diverse and customizable. Mechanical strength can be adjusted to be as low as that of LDPE or as high as that of strong aromatic polyester films (5, 6).

Apparent film properties Smooth-surfaced free-standing films were formed with all the biopolyesters by the thermo-compression method. Without plasticizers, rather flexible films were obtained with all the biopolyesters. PLA films were transparent and tough, PHBV and Ecoflex films were translucent with milk colored tint, and Biomax films were semitransparent and brittle. Ecoflex films were very soft and flexible with a rubber-like texture. Generally,

it is known that the formation and properties of biopolymer films are greatly affected by the processing methods used and the variety of thermo-mechanical history involved (11, 12). Table 2 shows the surface color and optical transparency of the films. The surface color of the films as determined by Hunter color values show that PHBV and Biomax films had a more green and yellowish tint (lower Hunter *a*- and higher Hunter *b*-values) than the other films. The optical transparency of biopolyester films was determined by measuring transmittance at 660 nm, and was significantly different ($p < 0.05$) depending on the biopolymer used. Though a little bit hazy, PLA film was the most transparent of the biopolyester films tested followed by Biomax, Ecoflex, and PHBV films. PLA film was even more transparent than LDPE film, i.e., the T value of PLA films (95.8%) was higher than that of LDPE film (92.6%). On the other hand, PHBV and Ecoflex films were almost opaque. The optical clarity of films is affected by additives, such as plasticizers or fillers, and the processing temperature (12). Therefore, the transparency of thermo-compressed biopolyester films can be improved by increasing the processing temperature within a range of temperature that will not degrade the polymer (11).

Tensile properties Table 3 shows the tensile properties of the biopolyester films with regard to thickness. Film thickness was dependent on the spreadability of biopolyesters during thermo-compression. The thickness of PHBV and Ecoflex films was about 1.6 times that of PLA and Biomax films. This indicates that PHBV and Ecoflex are less spreadable by thermo-compression and more cohesive than the other films. The tensile test results indicate that PLA film is the strongest and stiffest among the biopolyester films tested. Typically, TS measures strength, E measures flexibility, and EB measures film stiffness. PLA film is stronger than other commodity films such as LDPE (TS: 19-44 MPa) and PP (TS: 31-38 MPa) (15).

Table 3. Tensile properties of biopolymer films¹⁾

Film	Thickness (μm)	TS (MPa)	E (MPa)	EB (%)
PLA	97.6 \pm 4.7 ^a	40.98 \pm 1.12 ^c	1916.4 \pm 26.4 ^d	2.6 \pm 0.1 ^a
PHBV	155.2 \pm 4.0 ^b	19.00 \pm 0.20 ^b	561.0 \pm 19.3 ^c	6.3 \pm 0.2 ^a
Ecoflex	157.9 \pm 2.3 ^b	20.67 \pm 0.90 ^b	46.6 \pm 0.8 ^a	766.8 \pm 45.1 ^c
Biomax	92.4 \pm 3.0 ^a	11.03 \pm 1.28 ^a	121.7 \pm 32.4 ^b	0.03 \pm 0.04 ^a

¹⁾Means of three measurements \pm SD. Any two means in the same column followed by the same letter are not significantly different ($p > 0.05$) by Duncan's multiple range test.

Table 2. Hunter color values and optical transparency of biopolymer films¹⁾

Film	L	a	b	ΔE	T (%)
PLA	90.5 \pm 0.1 ^a	-0.99 \pm 0.01 ^c	-0.55 \pm 0.01 ^a	6.87 \pm 0.13 ^c	95.8 \pm 0.2 ^d
PHBV	90.9 \pm 0.1 ^b	-1.41 \pm 0.12 ^a	0.71 \pm 0.39 ^c	6.23 \pm 0.12 ^a	79.4 \pm 0.3 ^a
Ecoflex	90.8 \pm 0.1 ^{ab}	-1.09 \pm 0.04 ^c	-0.30 \pm 0.08 ^a	6.64 \pm 0.13 ^b	87.6 \pm 0.8 ^b
Biomax	90.5 \pm 0.1 ^a	-1.21 \pm 0.02 ^b	0.29 \pm 0.05 ^b	6.67 \pm 0.11 ^{bc}	91.5 \pm 0.3 ^c

¹⁾Means of three measurements \pm SD. Any two means in the same column followed by the same letter are not significantly different ($p > 0.05$) by Duncan's multiple range test.

However, the flexibility of PLA films was very low as shown by its low elongation at break (2.6%). PLA is known to possess good mechanical properties, clarity and processability, however its brittleness is a major drawback for many applications (16, 17). The strength of PHBV films was almost half of PLA films, and they also had low flexibility (EB: 6.3%). The strength of Ecoflex films was the same as PHBV films, but its E and EB values indicate that Ecoflex film is the most resilient and least stiff film tested. It is interesting to note that the EB of Ecoflex film (766.8%) is greater than those of LDPE (600%) and PP film (100-600%) (15). On the other hand, Biomax film was the weakest and the least flexible among the films tested, in addition to being the stiffest and most brittle.

The differences in the mechanical properties of these biopolyester films are mainly due to the chemical structure of the base biopolymer. Generally, film flexibility and gas barrier properties depend on the polymer structure, manufacturing process, physico-chemical conditions (i.e., temperature, pressure), and the presence of plasticizers and other additives (12, 18-21). Differences in processing parameters, such as temperature, pressure, and the use of solvent, may determine the extent of conformational changes, aggregation, and heat induced cross-linking that occur during the preparation of thermo-compression films.

Water vapor permeability (WVP) and water solubility (WS)

The WVP values, along with actual RH values at the underside of the films during testing, are shown in Table 3. The WVP values ranged from 1.26×10^{-11} g·m/m²·sec·Pa for PHBV film to 6.23×10^{-11} g·m/m²·sec·Pa for Ecoflex film. These results indicate that PHBV film is the most resistant to water vapor permeation followed by Biomax, PLA, and Ecoflex. It is important to note that the WVP value of PLA film agreed well with the results for extruded PLA films reported by Auras *et al.* (22). They reported that the WVP of PLA films, determined by Permatran W3/31 (Mocon Inc., Minneapolis, MN, USA), ranged from 1.48 - 2.20×10^{-11} g·m/m²·sec·Pa depending on the temperature and PLA resin type used. The WVP values of the biopolyester films tested in this study are similar to that of cellulose acetate (3.2×10^{-11} g·m/m²·sec·Pa), and are between those of natural protein and carbohydrate biopolymer films and those of polyolefin films such as PE and PP (14, 23). Though the WVP values of the biopolyester films are 50-100 times higher than those of polyolefin films such as PP and LDPE, they are

Table 4. Moisture content (MC), water vapor permeability (WVP), and water solubility (WS) of biopolymer films¹⁾

Film	MC (%)	WVP ($\times 10^{-11}$ g·m/m ² ·sec·Pa)	RH _i (%)	WS (%)
PLA	0.4±0.1 ^a	2.54±0.08 ^c	99.3±0.0 ^b	0.09±0.04 ^{ab}
PHBV	5.9±1.4 ^b	1.26±0.03 ^a	99.8±0.0 ^d	0.36±0.04 ^c
Ecoflex	0.0±0.0 ^a	6.03±0.15 ^d	99.0±0.0 ^a	0.14±0.03 ^b
Biomax	1.1±0.1 ^a	1.77±0.28 ^b	99.5±0.1 ^c	0.03±0.04 ^a

¹⁾Means of three measurements±SD. Any two means in the same column followed by the same letter are not significantly different ($p > 0.05$) by Duncan's multiple range test.

two orders of magnitude lower than those of carbohydrate or protein-based biopolymer films. The WVP values of polyolefins films determined at 38°C with a 0-90% RH gradient were reported as 0.049×10^{-11} g·m/m²·sec·Pa for PP and 0.07 - 0.097×10^{-11} g·m/m²·sec·Pa for LDPE (23).

We also observed that the actual RH values at the inner film surface were close to 100% for all the biopolyester films. This indicates that the water vapor pressure underneath the film is essentially the same as right above the water surface; therefore it is not necessary to account for the resistance of stagnant air layer between the film and water surface in the water vapor transmission rate measuring cups (11, 14).

The moisture content of biopolyester films was very low indicating that they are hydrophobic. This is also supported by the WS measurements. The WS of the biopolyester films was almost negligible indicating that they are highly water resistant. All biopolyester films maintained their integrity without swelling even after 24 hr of incubation in water at room temperature, i.e., they were not soluble in water. Such high water resistance properties of the biopolyester films makes them useful for many applications, including packaging, paper coating, or blending with other biopolymers, especially for packaging high-moisture foods.

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References

- Krochta JM, De Mulder-Johnston C. Edible and biodegradable polymer films: Challenges and opportunities. *Food Technol.* -Chicago 51: 61-74 (1997)
- Kaplan DL. Introduction to biopolymers from renewable resources. pp. 1-29. In: *Biopolymers from Renewable Resources*. Kaplan DL (ed). Springer-Verlag, Berlin, Germany (1988)
- Petersen K, Nielsen PV, Berteksen G, Lawther M, Olsen MB, Nilsson NH, Mortensen G. Potential of biobased materials for food packaging. *Trends Food Sci. Tech.* 10: 52-68 (1999)
- Lenz RW, Marchessault RH. Bacterial polyesters: Biosynthesis, biodegradable plastics and biotechnology. *Biomacromolecules* 6: 1-8 (2005)
- Mohanty AK, Misra M, Drzal LT, Selke SE, Harte BR, Hinrichsen G. Natural fibers, biopolymers, and biocomposites: An introduction. pp. 1-36. In: *Natural Fibers, Biopolymers, and Biocomposites*. Mohanty AK, Misra M, Drzal LT (eds). CRC Press, Inc., Boca Raton, FL, USA (2005)
- Clarival AM, Halleux J. Classification of biodegradable polymers. pp. 3-31. In: *Biodegradable Polymers for Industrial Applications*. Smith R (ed). CRC Press, Inc., Boca Raton, FL, USA (2005)
- Scholz C, Gross RA. Biopolyesters and biocatalysis introduction. pp. 1-11. In: *Polymers from Renewable Resources: Biopolyesters and Biocatalysis*. ASC Symposium Series 764. Scholz C, Gross RA (eds). American Chemical Society, Washington, DC, USA (2000)
- Debeaufort F, Quezada-Gallo JA, Voilly A. Edible films and coatings: Tomorrow's packagings: A review. *Crit. Rev. Food Sci.* 38: 299-313 (1998)
- Ryu SY, Rhim JW, Lee WJ, Yoon JR, Kim SS. Relationship between moisture barrier properties and sorption characteristics of edible composite films. *Food Sci. Biotechnol.* 14: 68-72 (2005)
- Rhim JW, Lee JH, Kwak HS. Mechanical and water barrier properties of soy protein and clay mineral composite films. *Food*

- Sci. Biotechnol. 14: 112-116 (2005)
11. Rhim JW, Mohanty AK, Singh SP, Ng PKW. Effect of processing methods on performance of polylactide (PLA) films: Thermo-compression and solvent casting methods. *J. Appl. Polym. Sci.* 101: 3736-3742 (2006)
 12. Cunningham P, Ogale AA, Dawson PL, Acton JC. Tensile properties of soy protein isolate films produced by a thermo-compression technique. *J. Food Sci.* 65: 668-671 (2000)
 13. Rhim JW, Gennadios A, Weller CL, Cezeirat C, Hanna MA. Soy protein isolate-dialdehyde starch films. *Ind. Crop Prod.* 8: 195-203 (1998)
 14. Gennadios A, Weller CL, Gooding CH. Measurement errors in water vapor permeability of highly permeable, hydrophilic edible films. *J. Food Eng.* 21: 395-409 (1994)
 15. Hernandez RJ, Selke SEM, Culter JD. Major plastics in packaging. pp. 89-134. In: *Plastics Packaging*. Hanser Gardener Publications, Inc., Cincinnati, OH, USA (2000)
 16. Garlotta D. A literature review of poly(lactic acid). *J. Polym. Environ.* 9: 63-84 (2001)
 17. Drumright RE, Gruber PR, Henton DE. Polylactic acid technology. *Adv. Mater.* 12: 1841-1846 (2000)
 18. Gällstedt M, Mattozzi A, Johansson E, Hedenqvist MS. Transport and tensile properties of compression-molded wheat gluten films. *Biomacromolecules* 5: 2020-2028 (2004)
 19. Mangavel C, Rossignol N, Perronnet A, Barbot J, Popineau Y, Guéguen J. Properties and microstructure of thermo-pressed wheat gluten films: a comparison with cast films. *Biomacromolecules* 5: 1596-1601 (2004)
 20. Redl A, Morel MH, Bonicel J, Vergnes B, Guilbert S. Extrusion of wheat gluten plasticized with glycerol: Influence of process conditions on flow behavior, rheological properties, and molecular size distribution. *Cereal Chem.* 76: 361-370 (1999)
 21. Orliac O, Rouilly A, Silvestre F, Rigal L. Effects of various plasticizers on the mechanical properties, water resistance, and aging of thermo-molded films made from sunflower proteins. *Ind. Crop Prod.* 18: 91-100 (2003)
 22. Auras R, Harte B, Selke SEM. Poly(lactide); a natural 'green' alternative for plastic packaging materials. Presented at the 4th International Plant Biomechanics Conference, Michigan State University, East Lansing, MI, USA (2003)
 23. Morillon V, Debeaufort F, Blond G, Capelle M, Voilley A. Factors affecting the moisture permeability of lipid-based edible films: A review. *Crit. Rev. Food Sci.* 42: 67-89 (2002)