



STARCH/CHITOSAN FILM FORMING HYDROGEL

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The objective of this study was to determine the effects of alkyl polyglucoside (APG) on the structural and physical properties of the films obtained from chitosan-lactate and starch/chitosan-lactate hydrogels. The adding of APG has been done to improve the spreadability of film forming solution on hydrophobic surfaces as vegetables, fruits, skin or hair. APG, biocompatible nonionic surfactant, was first used for this purpose. Starch/chitosan-lactate/APG films were prepared by hydrogel casting method. The wettability of starch/chitosan-lactate/APG hydrogels was evaluated by contact angle measurements. The contact angles of hydrogels on hydrophobic Teflon surface decreased with the APG concentration. The structure and physical properties of the formed films were studied by using swelling, X-ray diffraction, optical microscopy, mechanical testing, and differential scanning calorimetry. The physical characteristics of biopolymeric films depend on the starch/chitosan-lactate ratio, and the concentration of APG. X-ray diffraction analysis indicated that the chitosan-lactate and starch/chitosan-lactate films are crystalline and partially amorphous.

INTRODUCTION

Starch is a polysaccharide derived from plants that can be produced at low cost and large scale. Starch is abundant, edible, fully biodegradable, easily renewable, a low cost and a promising candidate for developing sustainable materials.^{1, 2} Application of pure starch films is still limited because of its brittleness and solubility in both hot and cold water.³ The mechanical properties of starch films were improved by incorporating the other polysaccharides and hydrophobic materials through blending, an effective way to prepare compatible materials. Recently, many researchers have extensively explored the development of starch composite films with other polymers such as collagen,⁴ poly(vinyl alcohol),⁵ carrageenan,⁶ gelatin,^{7, 8} lignin,⁹ egg albumen,¹⁰ chitosan^{11, 12} Because of the properties of the films obtained from chitosan and starch, they could be recommended in food packaging and medical applications.¹³

Chitosan, a major component of the crustacean shells, is a linear, crystalline polysaccharide consisting of β -(1 \rightarrow 4) linked N-acetyl-D-glucosamine (Poly-(1-4)-2-Amino-2-deoxy- β -D-Glucan. It has excellent film-forming ability and antimicrobial properties suitable for obtaining antimicrobial films.¹⁴ Chitosan has been found to be nontoxic, biodegradable, biocompatible^{15, 16} and may be easily combined with other materials.^{4, 11, 12} The fact that the positive electrical charge of chitosan allows it to combine with all parts of the skin and hair with negative electrical charge, counts at its application in pharmaceutical, medical, and cosmetic industries.¹⁷ The biopolymer is used as a film forming, antistatic, antibacterial and antifungal agent, to maintain moisture and tone of the skin, to treat acne, to protect the epidermis, to reduce static electricity in hair, to fight against dandruff, to improve the suppleness of the hair, to make the hair softer. Chitosan is used in shampoos, hair gels, as bacteria-inhibiting in tooth pastes and mouthwashes as well as a cationic film forming agent in skin care

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products¹⁸ and in food coating and packaging.^{14, 19} Chitosan could be an alternative to collagen or hyaluronic acid in skin care preparations.²⁰

Chitosan films were changed from rigid to flexible when the solvent, acetic acid solution was replaced by lactic acid solution.^{19, 21} Lactic acid could be used as a solvent for chitosan with applications in food coating, dermatology and cosmetic dermatology because it is a natural constituent of the human body. The facial mask containing chitosan, lactic acid and curcuminoids has been developed.²²

It is necessary to use a surfactant for improving the spreadability of a hydrophilic hydrogel on the hydrophobic surface.²³ Surfactants could be incorporated into the film formulation to reduce surface tension, improving the wettability and adhesion of the film. In this study, APG, a nonionic surfactant, was chosen for this purpose. APG is completely biodegradable and has excellent dermatological properties and synergistic effects with other surfactants.^{24, 25} APG could promote the antimicrobial activity of chitosan²⁶ and monitor the spreading of biopolymeric sessile droplets on the hydrophobic surfaces as vegetables, fruits, skin or hair.^{27, 28} Studies about the spreadability of starch/chitosan hydrogels enhanced by surfactants were not reported in the literature. However, studies regarding the effect of surfactants on individual starch²⁹ and chitosan³⁰ films have been published.

The main objective of this study was to evaluate the influence of APG on the spreadability on low-energy surfaces of chitosan-lactate and starch/chitosan-lactate hydrogels APG, nonionic surfactant was first used for this purpose. The second aim was to determine if the presence of APG spoil or not the structural and physical properties of the starch/chitosan-lactate films.

RESULTS AND DISCUSSION

The contact angle values from Fig. 1 indicate that the presence of APG reduces the contact angles of chitosan-lactate and starch/chitosan-lactate hydrogels on the surface of Teflon, and improves the spreading of biopolymeric hydrogels on hydrophobic surface. The spreadability of the film forming hydrogel on the object to be coated is very important that is why the interval of time necessary for the spreading operation must be minimal. This condition is well satisfied especially for the samples CHS1 and CHS2.

The chitosan-lactate and starch/chitosan-lactate films obtained by hydrogel casting on Teflon plate are compact, homogeneous and present a better flexibility than the purely starch film, which is brittle. To evaluate their microstructure, the blends have been analyzed by means of optical microscopy. The starch/chitosan-lactate/APG films present a macroporous structure (Fig. 2).

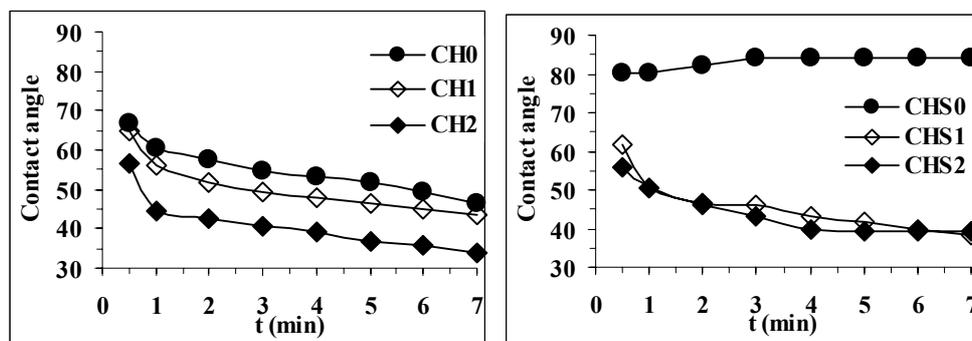


Fig. 1 – Contact angle of chitosan-lactate/APG and starch/chitosan-lactate/APG hydrogels on Teflon.

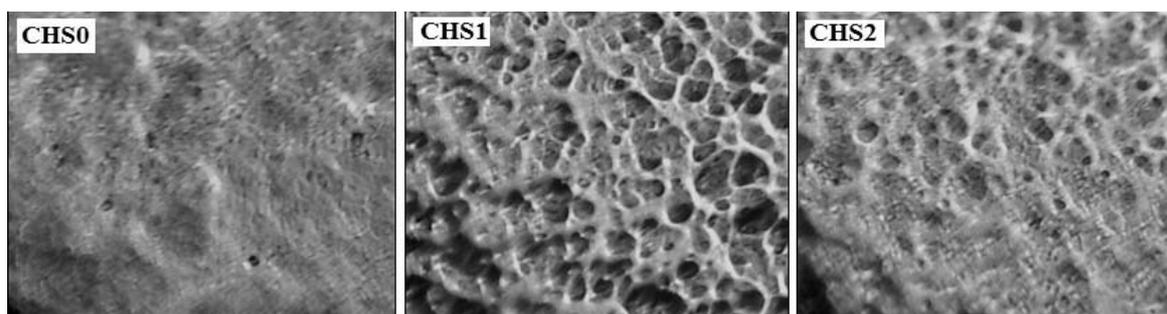


Fig. 2 – Optical microscopy of starch/chitosan-lactate/APG films.

The swelling capacity of chitosan-lactate/APG films calculated with equation (1) increases almost linear with APG concentration as can be seen in Fig. 3. The swelling capacities of biodegradable blend films are higher than those of the pure chitosan film. The highest sorption capacities are those of the blend film with 0.4% APG. Water is capable of diffusing through polymers and it is absorbed to different degrees depending on the molecular and microstructural characteristics of polymeric material. The porosity of starch/chitosan-lactate/APG films determines a higher swelling of the films.

The mechanical properties of chitosan-lactate and starch/chitosan-lactate films with and without APG have been compared. The thickness of the films, which varies from 0.03 to 0.055 mm has been used to calculate the tensile stress at break. The values of stress and strain at break for all the polymer films are shown in Fig. 4. The pure starch films are too brittle, therefore they are inadequate for use in many applications. The adding of

chitosan in the starch films improves their mechanical properties significantly. The increase in the tensile stress at break of the starch film after adding of chitosan indicates the presence of intermolecular interactions in the blend film.

The results demonstrate that starch/chitosan-lactate film with APG has a lower stress and elongation at the break when the surfactant is added. The addition of APG to starch/chitosan-lactate film leads to a reduction in stress at break and elongation at the break of film probably due to the strong steric effects of APG and to the fact that the polymer chains cannot slide freely past one another. However, the mechanical properties of the chitosan-lactate films are not significantly modified after the addition of the surfactant. Elongation at break is an indication of the film flexibility and stretch ability. The decrease in percentage elongation of chitosan and starch/chitosan films at the addition of surfactant is due to the forming of a heterogeneous film structure.

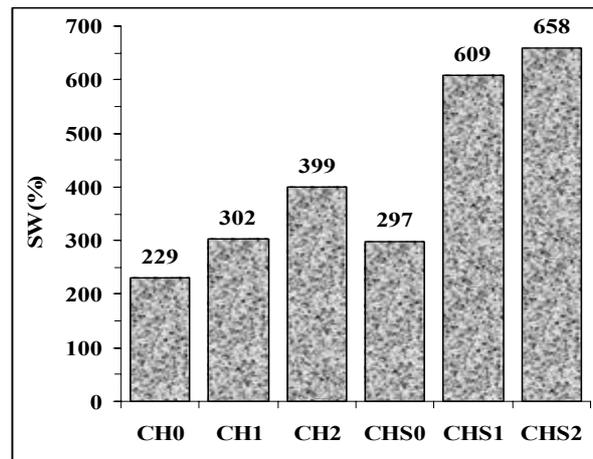


Fig. 3 – Sorption capacities of films in phosphate buffer at pH 7.4, within 30 minutes.

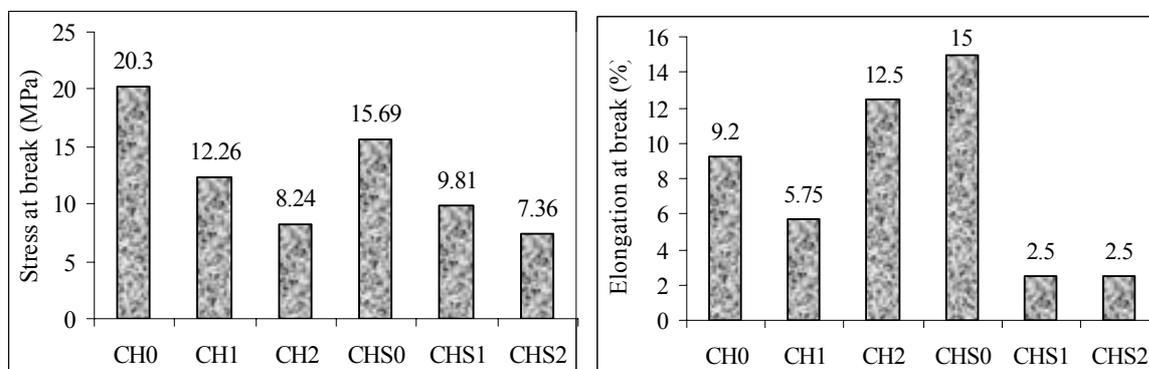
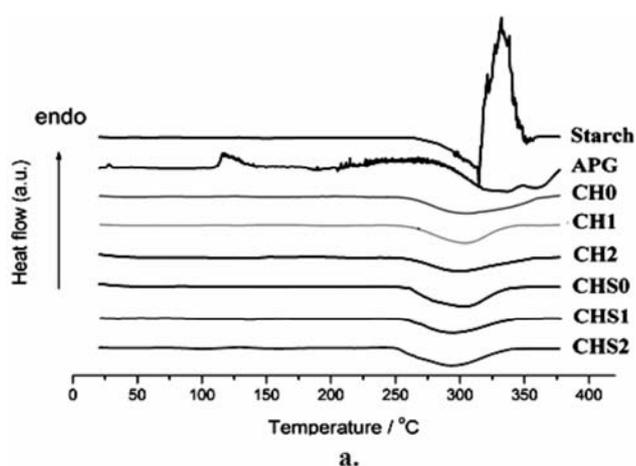


Fig. 4 – Mechanical properties: tensile strength and elongation at break of biodegradable films.

The DSC curves for chitosan, starch, APG, chitosan-lactate/APG and starch/chitosan-lactate/APG films are shown in Fig. 5. The exothermic peak that appears at temperature of 305°C in the DSC curve of chitosan can be attributed to the thermal decomposition. The DSC results show that adding of starch and APG to the chitosan causes a small decrease of the peak and onset temperatures of the thermal decomposition. The thermal decomposition process is detected in a wide temperature interval for all films. The films are found to be thermally stable under the temperature of 250°C. The DSC measurement shows that the onset temperature of thermal

decomposition of starch/chitosan-lactate/APG films decreases with increasing APG concentration. However, the thermal stability of chitosan and starch/chitosan films is not significantly changed at the addition of surfactant.

The XRD diffractograms of APG, chitosan-lactate film, and chitosan-lactate/APG films are shown in Fig. 6. These results indicate that all tested films are found to be crystalline with interspersed amorphous material. The broad peak indicates a random orientation of the crystallites in the film and it is characteristic of a predominantly amorphous phase.



Proba	$T_{\text{onset}}(^{\circ}\text{C})$	$T_{\text{peak}}(^{\circ}\text{C})$	$T_{\text{end}}(^{\circ}\text{C})$
CHO	261.38	305.16	366.41
CH1	259.52	302.77	345.00
CH2	256.83	298.13	359.26
CHS0	259.15	303.94	354.03
CHS1	256.15	293.92	347.25
CHS2	253.15	293.44	344.93

Fig. 5 – DSC curves of APG, chitosan, starch and starch/chitosan films (a) and the representative thermal data of the samples (b).

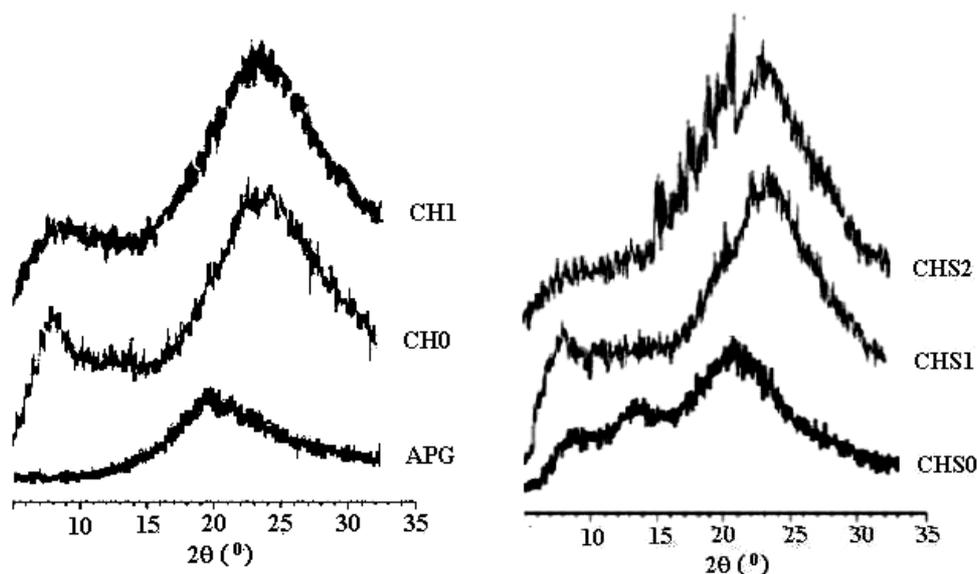


Fig. 6 – X-ray diffractograms of APG, chitosan film, and starch/chitosan films with and without surfactant.

From previous report²¹ the diffraction peak at around 21–22° (2θ) was observed in chitosan-acetate film. In our study, when the chitosan

solutions are prepared by using lactic acid, a broad peak appears in all chitosan and starch/chitosan films but it is shifted to a higher angle. This result

suggests that the acid used in preparing films affects their crystallinity, which may be due to the intermolecular interactions between free amino groups of chitosan and carbonyl groups of lactic acid. Niamsa et al.¹⁹ had evidenced these interactions by FTIR spectroscopy. The crystallinity of chitosan is affected by adding starch and APG to the film. The peaks at around 2θ value of 15°, 17°, 18° and 23° corresponding to the A-type pattern of cereal starch² can be identified in the diffractogram for starch/chitosan film with APG 0.4%. In this case, probably due to the crystallinity of starch which is increased in the blend film, the tensile strength and the extensibility are decreased. These results indicate that the mechanical properties of films are related to the network structure. Crystal peaks attributed to starch cannot be found in the pattern of the starch/chitosan film with APG 0.04%. APG has a relatively narrow peak at 19.78. The presence of APG surfactants modifies the shape of the crystallization peak and increases the crystallinity of starch/chitosan films, especially when the surfactant concentration is high. The formation of crystalline regions increases the rigidity of the films. A small increase in crystallinity of starch/chitosan film with APG is attended by a decrease in tensile properties, particularly the stress and the breaking elongation. The XRD data confirms the DSC results and indicate that APG and starch change the crystalline structure of chitosan.

EXPERIMENTAL

Materials. The biopolymers used in the experiments are commercial corn starch from Dr. Oetker Roumania and chitosan. Chitosan with medium molecular weight and a degree of deacetylation of 75-85%, was obtained from Aldrich. The surfactant APG (C12-C14) was purchased from Cospha, and lactic acid from Merck.

Hydrogel and film preparation. The chitosan-lactate solutions were prepared by dissolving the chitosan (2% w/v) in a 2% (v/v) lactic acid solution under magnetic stirring during 3 h at room temperature (25°C). APG was added to chitosan solution in concentration of 0.4% and 0.04%. Corn

starch was dispersed in water (2% w/v) and heated at 90°C for 30 minutes under continuous stirring to gelatinize completely. The gelatinized starch was then cooled at room temperature. The chitosan-lactate and the starch/chitosan-lactate hydrogel were obtained by mixing the chitosan and starch hydrogels followed by stirring for several hours. The films were obtained by casting technique: 10 g starch/chitosan hydrogel was dispensed on the surface of a rectangular Teflon plate (65-95 mm) and dried at room temperature for 72 h. A series of hydrogels based on chitosan and starch, with and without APG, were obtained and used to prepare biodegradable films. The weight ratios (wt) of starch and chitosan were: 0:1, 1:3, 1:1 and 3:1. The starch/chitosan films prepared at weight ratio of 1:1 and 3:1 were very brittle. In the present work, we have chosen to examine and analyze the following formulations: 0:1 and 1:3 weight ratio of starch to chitosan. The composition of biopolymeric hydrogels used in this study is presented in Table 1.

Contact angle measurements. The contact angles were determined by sessile drop method using a horizontal microscop with video camera. A drop of biopolymeric hydrogel was placed on the Teflon solid surface and the contact angles were determined from video camera images of the profile of sessile drops. The contact angle values were expressed as an average of 10 measurements.

Starch/Chitosan-lactate/APG film characterization. The digital images of the films were taken using Bresser Biolux-AL microscope with video-camera. The magnification of the objective lens used was 10X.

The water sorption capacities of the films were determined by soaking a known weight of film in phosphate buffer at pH 7.4 for 30 minutes. The weight of the wet film was determined by blotting the surface of the film with filter paper to remove excess water. The film was weighed immediately. The swelling capacity (%) was calculated from the equation:

$$SW = \frac{W_f - W_i}{W_i} \cdot 100 \quad (1)$$

where W_f is the weight of the film after 30 minutes of water sorption and W_i is the initial weight of the film. The SW values were expressed as an average of 3 measurements.

The mechanical properties were measured using a ZMG Schopper type Dynamometer. Dried films were peeled from the Teflon plate and cut in rectangles of about 80 mm by 10 mm. Film strip was held between two clamps positioned at a distance of 40 mm. The stress at break (applied force/initial cross-sectional area of film) and percentage elongation at break (increase in length of the film/initial length between the grips) for all polymer films were obtained by uniaxial tensile testing at 24°C. The film thickness was measured with a hand micrometer at five random locations on the film.

Table 1

Starch/Chitosan/APG hydrogel composition

Sample	Starch/Chitosan ratio (wt/wt)	APG % (wt/wt)	Sample	Starch/Chitosan ratio (wt/wt)	APG % (wt/wt)
CH0	0:1	-	CHS0	1:3	-
CH1	0:1	0.04%	CHS1	1:3	0.04%
CH2	0:1	0.4%	CHS2	1:3	0.4%

The X-Ray diffraction (XRD) quantitative analysis was performed using a DRON-2 diffractometer. The samples were scanned in the range of diffraction angle $2\theta = 1-35^\circ$. The interbasal spacing was calculated based on the Bragg's law.

The differential scanning calorimetry (DSC) measurements have been carried out on a Perkin Elmer Diamond DSC calorimeter under a heating rate of 10 K/min over a temperature range (20–400) °C in an inert atmosphere (He). The apparatus was calibrated for temperature and enthalpy by melting high purity indium. The samples of 1 to 4 mg were transferred into aluminum crucibles, which were sealed and weighed with the Partner XA balance with a precision of 10 µg.

CONCLUSIONS

The spreadability of starch/chitosan-lactate hydrogel on a hydrophobic surface such as Teflon, has been improved by the addition of APG. This behavior was sustained by lower values of the contact angles obtained for hydrogels with APG than those obtained in the absence of surfactant.

The physical characteristics of films formed by hydrogel casting depended on the concentration of APG. The highest swelling capacity of 658% was obtained for the starch/chitosan-lactate film with 0.4% APG. The incorporation of surfactant into the polymeric films led to a lower tensile strength. For starch/chitosan-lactate film, the percentage of elongation at break decreased from 15% to 2.5% when surfactant was added. X-ray diffraction analysis indicated that the biopolymeric films were not completely amorphous, but partially crystalline. X-ray diffraction data revealed the existence of interactions between the polymers and surfactant, which are in accordance with the results obtained from testing the mechanical properties of the starch/chitosan-lactate/APG films. Thermal stability of the starch/chitosan-lactate films with APG did not decrease dramatically, the films remaining stable at temperatures below 250°C.

REFERENCES

- J.-F. Zhang and X. Z. Sun, *Biomacromolecules*, **2004**, *5*, 1446-1451.
- C. Primo-Martín, N.H. Van Nieuwenhuijzen, R.J. Hamer and T. Van Vliet, *J.Cereal Sci.*, **2007**, *45*, 219-226.
- S. Mali, M. V. E. Grossmann, M. A. Garcia, M. N. Martino and N. E. Zaritzky, *J. Food Eng.*, **2006**, *75*, 453-460.
- V.-N. Stănescu, M. Olteanu, M. Florea-Spiroiu and Z. Vuluga, *Rev. Roum.Chim.*, **2009**, *54*, 767-771.
- B. Ramaraj, *J. Appl. Polym. Sci.*, **2007**, *103*, 1127-1132.
- G. Savary, S. Handschin, B. Conde-Petit, N. Cayot and J.-L. Dublier, *Food Hydrocolloid*, **2008**, *22*, 520-530.
- M. A. Aguilar-Méndez, E. San Martín-Martínez, S. A. Tomás, A. Cruz-Orea and M. R. Jaime-Fonseca, *J. Sci. Food Agr.*, **2008**, *88*, 185-193.
- I. Arvanitoyannis, A. Nakayama and S.-I. Aiba, *Carbohydr. Polym.*, **1998**, *36*, 105-119.
- J. C. Vengal and M. Srikumar, *Trends Biomater. Artif. Organs*, **2005**, *18*, 237-241.
- S. Wongsasulak, T. Yoovidhya, S. Bhumiratana, P. Hongsprabhas, D. J. McClements and J. Weiss, *Food Res. Int.*, **2007**, *40*, 249-256.
- Y. X. Xu, K. M. Kim, M. A. Hanna and D. Nag, *Ind. Crop. Prod.*, **2005**, *21*, 185-192.
- W. Ban, J. Song, L. A. Lucia and D. S. Argyropoulos, *J. Appl. Polym. Sci.*, **2006**, *100*, 2542-2548.
- F. Liu, B. Qin, L. He and R. Song, *Carbohydr. Polym.*, **2009**, *78*, 146-150.
- P. K. Dutta, Shipra Tripathi, G.K. Mehrotra and J. Dutta, *Food Chem.*, **2009**, *114*, 1173-1182.
- H. K. No, S.P. Meyers, W.Prinyawiwatkul and Z. Xu, *J.Food Sci.*, **2007**, *72*, 87-100.
- R. Jayakumar, N. T. Nwe, S. Tokura and H. Tamura, *Int. J. Biol. Macromol.*, **2007**, *40*, 175-181.
- A. Chenite, M. Buschmann, D. Wang, C. Chaput and N. Kandani, *Carbohydr. Polym.*, **2001**, *46*, 39-47.
- H. Lautenschlager, *Kosmetische Praxis*, **2009**, *4*, 12-15.
- N. Niamsa and Y. Baimark, *Am. J. Food Technol.*, **2009**, *4*, 162-169.
- J. D. Dee, O. Rhode and R. Wachter, *Cosmet. Toiletries*, **2001**, *116*, 39-42.
- G. C. Ritthidej, T. Phaechamud and T. Koizumi, *Int. J. Pharm.*, **2002**, *232*, 11-22.
- J. Euasathien, C. Eamtawecharum, P. Benjasirimingkol, S. Soiputtan, P. Toprasri, T. Phaechamud and S. Nawanooparatsakul, *Silpakorn Univ. Int. J.*, **2005**, *5*, 140-147.
- M. Carneiro-da-Cunha, M. Cerqueira, B. Souza, M. Souza, J. Teixeira and A. Vicente, *J. Food Eng.*, **2009**, *95*, 379-385.
- J. Y. Kim, Y. A. Woo, H. J. Kim and J. D. Kim, *J. Pharm. Biomed. Anal.*, **2001**, *26*, 73-78.
- O. Cinteza and M. Dudau, *J. Surfactants Deterg.*, **2003**, *6*, 259-264.
- H. Liu, Y. Du, X. Wang, Y. Hu and J. F. Kennedy, *Carbohydr. Polym.*, **2004**, *56*, 243-250.
- H. Schott, *J. Pharm. Sci.*, **1971**, *60*, 1893-1895.
- R. A. Lodge and B. Bhushan, *J. Appl. Polym. Sci.*, **2006**, *102*, 5255-5265.
- M. Rodriguez, J. Osés, K. Ziani and J. I. Mate, *Food Res. Int.*, **2006**, *39*, 840-846.
- K. Ziani, J. Osés, V. Coma and J. I. Mate, *LWT – Food Sci. Technol.*, **2008**, *41*, 2159-2165.