SELECTED PHYSICAL MODIFICATION TECHNIQUES TO IMPROVE MECHANICAL PROPERTIES OF BIOPOLYMER-BASED PACKAGINGS: A BRIEF REVIEW

*Sakamon DEVAHASTIN[1], Wasina THAKHIEW[2] and Somchart SOPONRONNARIT[3]

[1]*Department of Food Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, 126 Pracha u-tid Road, Bangkok 10140, Thailand*

[2]*Department of Nutrition, Faculty of Public Health, Mahidol University, 420/1 Rajavithi Road, Bangkok 10400, Thailand*

[3]*Energy Technology Division, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi, 126 Pracha u-tid Road, Bangkok 10140, Thailand*

Corresponding author: Sakamon DEVAHASTIN. E-mail: sakamon.dev@kmutt.ac.th

ABSTRACT

Despite their advantages in terms of health and environmental friendliness, biopolymer-based food packagings exhibit inferior mechanical properties, especially their ability to elongate, to their synthetic counterpart. Considerable attempts have therefore been made to improve the mechanical properties of biopolymer-based packagings. While several alternatives are plausible and have been explored, physical modifications have attracted much interest as they involve no (or minimal) use of additives and hence are relatively inexpensive to implement. In this presentation, a brief review of selected techniques that have been utilized to improve the mechanical properties of biopolymer-based packagings is given; chitosan is discussed as the test biopolymer. These include the use of advanced drying technologies to prepare films from a suitably plasticized film-forming solution. Various homogenization technologies to prepare film-forming solutions that exhibit better blending between a polymer base solution and plasticizer are also discussed. Mechanical properties improvement is presented along with the changes in the polymer structural and rheological properties to highlight the interrelationships between these properties.

INTRODUCTION

In recent years, more attention has been given towards biopolymer packagings, especially packaging films, as they are environmentally friendly and naturally biode-gradable. However, the nature of biopolymer packaging films, which is rigid and brittle, causes limitations in their food applications [1]. Several schemes to improve the mechanical properties of biopolymer-based films have been explored. Among the possible alternatives, use of advanced drying technolo-gies to prepare films is promising.

Another widely used alternative to improve the mechanical properties of biopolymer-based films, especially to increase the percent elongation of the films, is addition of an appropriate type and concentration of plasticizer to a filmforming solution prior to solvent evaporation (i.e., drying) to cast the films. Plasticizer is believed to interfere with the polymer chains, decreasing the intra and intermolecular forces, while increasing the free volume or facilitating the mobility of the chains and hence the enhanced flexibility and stretchability of the films [2-4]. Since the principal mechanism of plasticization is based on interfering with the polymer chains, any means that can help disperse a plasticizer in a film-forming colloidal system is desirable. A variety of homogenization techniques can be used for such a purpose.

In this paper, a brief review on the use advanced drying technologies to prepare films from a suitably plasticized film-forming solution is given. Selected results on the use of various homogenization techniques to prepare film-forming solutions that exhibit better blending between a polymer base solution and plasticizer are also discussed. Mechanical properties improvement is presented along with the changes in the polymer structural and rheological properties to highlight the interrelationships between these properties.

USE OF ADVANCED DRYING TECHNOLOGIES TO PREPARE FILMS

A number of researchers have investigated the use of different drying techniques to prepare films as it is well recognized that drying methods and conditions affect the properties and functionalities of the films. Mayachiew and Devahastin [5], for example, investigated the

effects of different drying methods and conditions, i.e., ambient drying (~30 oC), hot air drying at 40 oC, vacuum drying and lowpressure superheated steam drying (LPSSD) within the temperature range of 70-90 oC at an absolute pressure of 10 kPa, on the physical and mechanical properties of chitosan films. Selected results of their work are given in Table 1.

It is seen in Table 1 that the maximum value for tensile strength was observed in the case of LPSSD at 70 oC. This might be due to the effects of higher degrees of crystallinity and thermal crosslinkage that occurred at this condition. From the result of the X-ray diffraction analysis (Fig. 1), chitosan films with the higher degrees of crystallinity (LPSSD and ambient dried films) exhibited higher tensile strength when the only factor, i.e., crystallinity of the films, was considered. However, the tensile strength of LPSSD films was higher than that of ambient dried films because the drying temperature of LPSSD was higher, thus inducing more thermal crosslin-kage within the LPSSD films. The percent elongation of LPSSD films was also the highest. Drying temperature did not significantly affect the percent elongation.

Table 1. Mechanical properties of chitosan films (Modified from Mayachiew and Devahastin [5])

Drying condition	Tensile strength (MPa)	Percent elongation
Control		
~ 30°C	38.7±2.4^{cd}	24.6±3.8^{de}
40°C	34.9±3.4^{bcd}	23.7±2.8^{de}
Vacuum drying		
70°C	30.9±3.8^{ab}	20.2±4.4^{bcde}
80°C	27.0±2.4^{ab}	19.8±2.5^{abcd}
90°C	27.2±4.0^{ab}	19.7±3.1^{abcd}
LPSSD		
70°C	69.0±2.8^{f}	24.9±2.5^{e}
80°C	65.8±3.4^{f}	25.1±4.4^{e}
90°C	50.2±4.7^{e}	24.8±3.5^{e}

Different superscripts within the same column mean that the values are significantly different ($p < 0.05$)

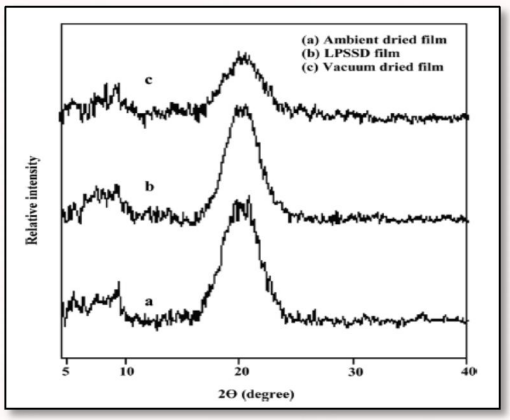

Fig. 1 X-ray diffraction patterns of chitosan films dried by ambient drying at ~ 30 ºC; LPSSD at 70 ºC and vacuum drying at 70 ºC [5]

Thakhiew et al. [6] later investigated the combined use of glycerol as a plasticizer and hot air drying at 40 ºC, vacuum drying and low-pressure superheated steam drying (LPSSD) at 90 ºC, 10 kPa to prepare chitosan films. In the case of hot air drying, the expected decrease in the tensile strength and increase in the percent elongation with increasing plasticizer concentr-ation was observed. On the other hand, in the cases of vacuum drying and LPSSD, glycerol did not exhibit the conventional effect at the concentrations of 25-125% w/w; the tensile strength and percent elongation of the films plasticized at these glycerol concentrations were not significantly different. This might be due to the higher degrees of crystallinity and thermal cross-linkage that occurred more in the films during these two drying processes [5]. Higher degrees of crystallinity and thermal cross-linkage resulted in increased intermo-lecular and intramolecular forces in the polymer chain and hence more limited chain mobility. Vacuum and LPSSD dried films were then more compact. Glycerol phase separation was another possible reason for such an observed phenome-non.

USE OF HOMOGENIZATION TECHNIQUES TO PREPARE FILM-FORMING SOLUTIONS

As mentioned earlier, since the principal mechanism of plasticization is based on interfering with the polymer chains, any means that can be applied to disperse a plasticizer in a film-forming colloidal system is desirable. A variety of homogenization techniques can be used for such a purpose. Rotor-stator homo-genization is among the possible options [7].

High-pressure homogenization is another possible alternative that has been commonly used to emulsify, disperse and reduce the size of disperse phase droplets in a colloidal system [7-8]. High-pressure homogenization not only affects the dispersed phase, but also the macromolecules and hence the structure and functional properties of the resulting biopolymer films [9]. Smaller plasticizer droplet size achieved via the use of highpre-ssure homogenization helps increase the plasticization ability [1]. The reduced size of biopolymer might have also resulted in the higher uniform matrices of the obtained films [10].

Thakhiew et al. [11] recently investigated possible improvement of the mechanical properties of chitosan films via the use of different homogenization techniques to disperse glycerol in the chitosan film-forming solution. Rotor-stator homogenization at 9,600 rpm at atmospheric pressure and two-stage high-pressure homogenization at a gauge pressure of either 10/5, 20/5 or 30/5 MPa were tested. The prepared film-forming solutions were then dried by hot air drying at 40°C. Selected results are listed in Table 2.

Table 2. Mechanical properties of chitosan films prepared from differently treated film-forming solutions. Numbers in parentheses are percentage changes as compared to values belonging to control sample (Modified from Thakhiew et al. [11])

Condition	Tensile strength (MPa)	Percent elongation (%)
Without homogenization (control)	37.8 ± 1.3^{b}	28.7 ± 2.2^{a}
Rotor-stator homogenization	38.5 ± 2.9^{b} (2%)	29.1 ± 1.5^{a} (1%)
High-pressure homogenization (10/5 MPa)	46.4 ± 2.9^{cd} (23%)	35.9 ± 2.6^{de} (25%)
High-pressure homogenization (20/5 MPa)	34.6 ± 3.1^{ab} (-8%)	36.3 ± 0.8^{e} (26%)
High-pressure homogenization (30/5 MPa)	33.1 ± 5.2^{a} (-12%)	37.1 ± 4.2^{e} (29%)

Different superscripts within the same column mean that the values are significantly different ($p < 0.05$)

The influence of the structural change on the mechanical properties of the films is illustrated via the dynamic mechanical analysis (DMA) patterns of Fig. 2, which display the relationship between the storage modulus, loss modulus and tan δ of the films as a function of the temperature (in the range of -120 to 230 °C). In general, a more compact film structure would lead to an increase in the storage modulus due to more restricted chain mobility, resulting in a decrease in the percent elongation of a film [12]. As is seen in Fig. 2 the films prepared from the non-homogenized solutions exhibited the highest storage modulus; this was followed in descending order by the films prepared from rotor-stator and high-pressure homogenized solutions. This trend of the results is in agreement with that in Table 2. This is probably because the energy generated during high-pressure homogeni-zation was sufficient to decrease the size of glycerol droplets [13-15]. Smaller droplets could increase plasticization ability of the chitosan chains. An increase in the homogeni-zation pressure did not influence the percent elongation, however.

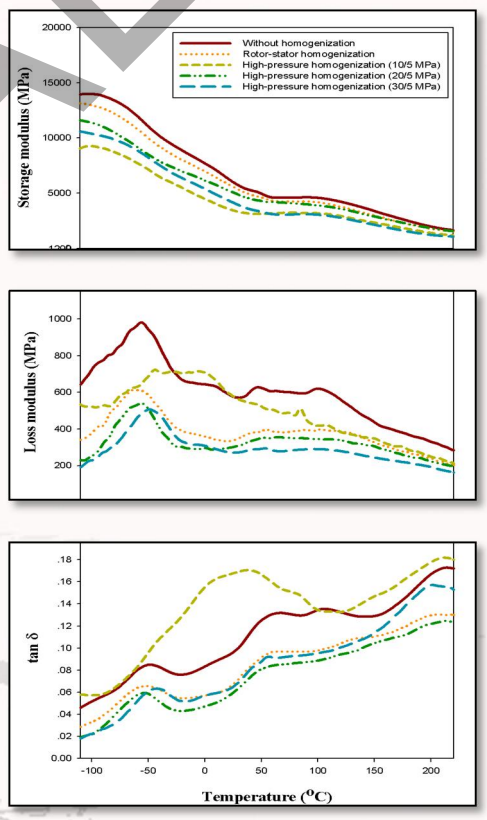

Fig. 2 Storage modulus, loss modulus and tan δ of chitosan films prepared from differently treated film-forming solutions [11]

The denser structure of the films led to an increase in the loss modulus because this type of structure possesses higher ability to dissi-pate energy, resulting in an increase in the tensile strength of the films [12]. As is seen in Fig.2 the

films prepared from the non-homogenized, rotor-stator homogenized and high-pressure homogenized solutions at 10/5 MPa possessed higher loss modulus than the films prepared from high-pressure homogen-ized solutions at 20/5 and 30/5 MPa. This trend of the results is again in agreement with the data in Table 2. The tensile strength decreased with an increase in the pressure due probably to the intense mechanical forces produced during the high-pressure homogenization, leading in turn to the degradation of the polymer chains [7, 15].

Rotor-stator homogenization could not induce the change of the tensile strength, percent elongation and degree of crystallinity of the films. On the other hand, high-pressure homogenization at 10/5 MPa could improve the tensile strength of the films by about 23%, while high-pressure homogenization at 20/5 and 30/5 MPa reduced the tensile strength of the films by about 8 and 12% when compared with the values of the control films, respectively. High-pressure homogenization improved the percent elongation and reduced the degree of crystallinity of the films by 25-29% and 40-47% when compared with the values of the control films, respectively.

CLOSING REMARKS

This paper briefly reviews some recent advances in applying physical methods to improve the mechanical properties of biopolymer films, in particular chitosan-based films. Use of advanced drying technologies, e.g., low-pressure superheated steam drying, can help improve the tensile strength of the films without sacrificing the percent elongation.

Use of high-pressure homogenization to produce smaller droplets of plasticizer can help increase the plasticization ability and emulsion stability by allowing better insertion of plasticization droplets between the polymer chains and hence more chain lubrication. This in turn leads to higher stretchability of the resulting films.

A study to further improve the emulsion stability of a film-forming solution as well as to find a way to modify the molecular structure of a base polymer is suggested.

ACKNOWLEDGEMENTS

The authors express their sincere appreciation to the National Science and Technology Development Agency (NSTDA), Thailand through its Research Chair Grant for the continued support of the study.

REFERENCES

[1] Sothornvit, R. and Krochta, J.M. Plasticizer effect on mechanical properties of β-lactoglobulin films. J. Food Eng. 50: 149-155 (2001)

[2] Abdorreza, M.N., Cheng, L.H. and Karim, A.A. Effects of plasticizers on thermal properties and heat sealability of sago starch films. Food Hydrocolloids. 25: 56-60 (2011)

[3] Aguirre, A., Borneo, R. and León, A.E. Properties of triticale protein films and their relation to plasticizing-antiplasticizing effects of glycerol and sorbitol. Ind. Crops Prod. 50: 297-303 (2013)

[4] Sothornvit, R. and Krochta, J.M. Plasticizer effect on oxygen permeability of β-lactoglobulin films. J. Agric. Food Chem. 48: 6298-6302 (2000)

[5] Mayachiew, P. and Devahastin, S. Comparative evaluation of physical properties of edible chitosan films prepared by different drying methods. Drying Technol. 26: 176-185 (2008)

[6] Thakhiew, W., Devahastin, S. and Soponronnarit, S. Effects of drying methods and plasticizer concentration on some physical and mechanical properties of edible chitosan films. J. Food Eng. 99: 216-224 (2010)

[7] Ma, W., Tang, C., Yin, S., Yang, X., Qi, J. and Xia, N. Effect of homogenization conditions on properties of gelatine-olive oil composite films. J. Food Eng. 113: 136-142 (2012)

[8] Fu, Z., Wang, L., Li, D., Wei, Q. and Adhikari, B. Effects of high-pressure homogenization on the properties of starch-plasticizer dispersions and their films. Carbohydr. Polym. 86: 202-207 (2011)

[9] Roesch, R.R. and Corredig, M. Texture and microstructure of emulsions prepared with soy protein concentrate by high-pressure homogeniza-tion. LWT – Food Sci. Technol. 36: 113-124 (2003)

[10] Kang, H.J. and Min, S.C. Potato peel-based biopolymer film development using high-pressure homogenization, irradiation, and ultrasound. LWT – Food Sci. Technol. 43: 903-909 (2010)

[11] Thakhiew, W., Champahom, M., Devahastin, S. and Soponronnarit, S. Improvement of mechanical properties of chitosan-based films via physical treatment of film-forming solu-tion. J. Food Eng. [In Press] (2015)

[12] Thakhiew, W., Devahastin, S. and Soponron-narit, S. Physical and mechanical properties of chitosan films as affected by drying methods and addition of antimicrobial agent. J. Food Eng. 119: 140-149 (2013)

[13] Fabra, M.J., Pérez-Masiá, R., Talens, P. and Chiralt, A. Influence of the homogenization conditions and lipid self-association on properties of sodium

caseinate based films containing oleic and stearic acids. Food Hydrocolloids. 25: 1112-1121 (2011)

[14] Matsakidou, A., Biliaderis, C.G. and Kioss-eoglou, V. Preparation and characterization of composite sodium caseinate edible films incorporating naturally emulsified oil bodies. Food Hydrocoll-oids. 30: 232-240 (2013)

[15] Vargas, M., Perdones, Á., Chiralt, A., Cháfer, M. and González-Martínez, C. Effect of homogenization conditions on physicoche-mical properties of chitosan-based film-forming dispersions and films. Food Hydro-colloids. 25: 1158-1164 (2011)