การศึกษาสมบัติทางความร้อนและสมบัติเชิงกลของแผ่นฟิล์มพอลิเบนซอกซาซีนผสมไคซาน

Thermal and Mechanical Properties of Biobased Chitosan/Polybenzoxazine Cross-Linked Films

กานต์สิริ ปักเคชาติ,[1*] สุจิตรา วงศ์เกษมจิตต์,[2] ยอดธง ใบมาก[1]

Kansiri Pakkethati,[1*] Sujitra Wongkasemjit,[2] Yodthong Baimark[1]

บทคัดย่อ

การสังเคราะห์พอลิเบนซอกซาซีนผสมไคโตซาน (น้ำหนักโมเลกุล 15,000 กรัม/โมล และ 100,000 กรัม/โมล) ในอัตราส่วน (พอลิเบนซอกซาซีน:ไคโตซาน)0:100, 20:80, 40:60, 50:50, 60:40, 80:20, 100:0น้ำหนักโมเลกุลของไคโตซานและอัตราส่วนผสมส่งผลต่อการขึ้นรูปเป็นแผ่นฟิล์มพอลิเมอร์เบนซอกซาซีน อัตราส่วนที่เหมาะสมในการขึ้นรูปแผ่นฟิล์มของไคโตซานน้ำหนักโมเลกุล 15,000 กรัม/โมล คือ 40:60 เนื่องจากแผ่นฟิล์มที่ได้มีพื้นผิวที่เรียบ ทั้งสังเกตด้วยตาเปล่าและผ่านการตรวจสอบสัณฐานวิทยาของแผ่นฟิล์มด้วยเครื่องกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด สำหรับแผ่นฟิล์มผสมที่ใช้ไคโตซานน้ำหนักโมเลกุล 100,000 กรัม/โมล พบว่าแผ่นฟิล์มที่อัตราส่วน 60:40 มีคุณภาพทางสัณฐานวิทยาที่ดี สมบัติทางความร้อนและสมบัติเชิงกลของแผ่นฟิล์มถูกตรวจสอบด้วยเทคนิคการศึกษาเสถียรภาพทางความร้อนและการทดสอบแรงดึงในทิศทางเดียว พบว่าอัตราส่วน 50:50 ของไคโตซานน้ำหนักโมเลกุล 100,00 กรัม/โมล มีเสถียรภาพทางความร้อนที่ดี และมีความยืดหยุ่นสูงเมื่อเปรียบเทียบกับอัตราส่วนอื่นๆ จึงสรุปได้ว่าการผสมระหว่างพอลิเบนซอกซาซีนและไคโตซานส่งผลให้สมบัติทางความร้อนและสมบัติเชิงกลของแผ่นฟิล์มดีขึ้น ซึ่งจะก่อให้เกิดประโยชน์ในการนำไปใช้ต่อไป

คำสำคัญ: พอลิเบนซอกซาซีน ไคโตซาน สมบัติทางความร้อน สมบัติเชิงกล

Abstract

Synthesized polybenzoxazine was mixed with chitosan (Mw=15000 g/mol and Mw=100000 g/mol) at 0:100, 20:80, 40:60, 50:50, 60:40, 80:20, 100:0 ratio. The average molecular weight and the ratio affected polymer to form polymer film. The optimum ratio polybenzoxazine:chitosan (Mw=15000 g/mol) film was 40:60 which showed good morphology in SEM (scanning electron microscopy) and naked-eye results. For polybenzoxazine cross-linked with chitosan (Mw=100000 g/mol) film present good quality with 60:40 ratio. The thermal and mechanical properties of polymer films were characterized by using Thermogravimetric Analysis (TGA) and uniaxial tensile test. The best ratio of polybenzoxazine cross-linked chitosan

[1] ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหาสารคาม ตำบลขามเรียง อำเภอกันทรวิชัย จังหวัดมหาสารคาม 44150

[2] วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย ปทุมวัน กรุงเทพ 10330

[1] Department of Chemistry Faculty of Science Mahasarakham University Kantarawichai District Mahasarakham 44150 Thailand

[2] The Petroleum and Petrochemical College Chulalongkorn University PathumwanBangkok 10330, Thailand

[*]Corresponding author:KansiriPakkethati, Department of Chemistry Faculty of Science Mahasarakham University Kantarawichai District Mahasarakham 44150 Thailand

(Mw=100000 g/mol) film was 50:50 which showed good thermal stability and high flexibility compared with other ratio. It can be concluded that improvement of thermal and mechanical properties of film was successful by cross-linking between polybenzoxazine and chitosan.

Keywords: Polybenzoxazine, Chitosan, Thermal property, Mechanical property

Introduction

Nowadays, biodegradable polymer was interested and studied according to easily degradation, environmentally friendly material and excellent properties. Among the natural biodegradable polymers, chitosan has been actively developed and used in many fields during the past few decades.[1,2] Chitosan is branched polysaccharide and modified high molecular weight produced by deacetylation of chitin obtained from crab and shrimp shells. Chitin is the second most available natural biodegradable polymer on Earth after cellulose.[3] Chitosan has amino group ($-NH_2$) in substituent position caused chitosan can be dissolved in dilute acidic aqueous solutions. Due to its high chemical reactivity, good properties and low cost, chitosan has been widely used in various applications such as medicine, food, wastewater treatment and agriculture.[3,4] However, chitosan has some drawbacks, such as insolubility in organic solvents, brittle material as well as poor thermal and mechanical properties. These problems are commonly solved by grafting or cross-linking chitosan with other polymers.

Polybenzoxazine is one class of recently developed thermosetting polymers which are different from traditional polymers by their properties such as good mechanical strength, high thermal stability, good chemical and electrical resistance, low dielectric properties, and good chemical reactivity toward other polymers.[5-9] Benzoxazine monomers are heterocyclic compounds, discovered by Holly and Cope[10] in 1944 by using condensation reaction of a primary amine with formaldehyde and phenol. Polybenzoxazine is obtained via thermally activated ring-opening polymerization of benzoxazine monomers without using an initiator or catalyst. There are no toxic volatiles, harsh materials, or byproducts generated during the polymerization.[5,7,11,12] Recently, the development of polymer properties is much attention in cross-linking good properties of polymer with biodegradable polymer in order to improve the poor properties of biodegradable polymer. In this study, chitosan was developed the thermal and mechanical properties by cross-linking with polybenzoxazine.

Materials and Methods

Analytical grade 1,4-Dioxane was purchased from labscan, Ireland. Bisphenol-A (BPA, 97% purity) was obtained from Aldrich, Germany. Formaldehyde (analytical grade, 37%wt in water) and acetic acid were purchased from Merck, Germany. Triethylenetetramine (85% purity) was purchased from Fluka, Switzerland. Chitosan with Mw=15000 g/mol (90% DAC) and chitosan with Mw=100000 g/mol (95% DAC) were obtained from

Seafresh Chitosan (lab) Company Limited. All chemicals were used as received.

The film morphology was investigated using a scanning electron microscope (SEM, JEOL JSM-6460LV). A thermogravimetric analyzer (TGA, TA-Instrument TG SDT Q600) was used to investigate the thermal stability of films using a heating rate of 20 °C/min under a N_2 flow. The tensile properties of films were measured by using LLOYD Instrument at a crosshead speed of 10 mm/s. The results of each sample were determined from an average of at least 5 tests.

The benzoxazine was prepared by mixing bisphenol-A, formaldehyde and diamine (TETA) at a mole ratio of 1:4:1, respectively.[13] Firstly, bisphenol-A (6.84 g, 30 mmol) was dissolved in 1,4-dioxane (15 mL) in a 50 mL glass bottle and was stirred until a clear solution was obtained. A formaldehyde solution (9.73 g, 324 mmol) was then added to the bisphenol-A solution. The temperature was kept under 10 °C by using an ice bath. TETA was then added dropwise into the mixture while continuously stirring for approximately 1 hour until a transparent yellow viscous liquid was obtained.[14] The producing solution was precipitated in deionized water and dried under vacuum at room temperature for 24 hours.

Polybenzoxazine cross-linked chitosan films were prepared with various weight ratios: (100:0), (80:20), (60:40), (50:50), (40:60), (20:80), and (0:100) of polybenzoxazinewith TETA as diamine (PBZ-TETA):chitosan (CTS). A specified amount of chitosan was dissolved in 1.5% acetic acid solution under continuous magnetic stirring at ambient condition. At the same time, a desire amount of benzoxazine was also dissolved in 1.5% acetic acid solution by using a magnetic stirrer at room temperature. After completely dissolved of both polymers, the chitosan solution was slowly added to the benzoxazine solution under vigorous agitation by magnetic stirrer until a homogeneous mixture was obtained. The solution was poured onto a polystyrene dish and dried at 40 °C for 24 hour. Finally, the cross-linked films were obtained in difference color depending on the polybenzoxazine and chitosan ratio.

Results and Discussion

Morphology Analysis

Benzoxazineprecursor was successfully derived from the reation of bisphenol-A, TETA, and formaldehyde at a molar ratio of 1:1:4 via a quasi-solventless. All cross-linked polymer showed transparency films. Polybenzoxazine (PBZ-TETA) and chitosan (CTS) were prepared to be dense films.[14] However polybenzoxazine blended with chitosan in high average molecular weight (Mw=100000 g/mol) could be formed good morphology films compared to blend polybenzoxazine with low average molecular weight. The polymer ratio also affected to the appearances of polybenzoxazine cross-linking chitosan as shown in Table 1. PBZ-TETA:CTS (Mw=15000 g/mol) 80:20 film cannot be formed. PBZ-TETA:CTS (Mw=15000 g/mol) 40:60 ratio and PBZ-TETA:CTS (Mw=15000 g/mol) 60:40 ratio showed imperfect films.

Table 1 PBZ-TETA : CTS ratio and appearances of polybenzoxazine/chitosan films

PBZ-TETA : CTS	Appearances of films	
	CTS (Mw = 15000)	CTS (Mw = 100000)
0:100		
20:80		
40:60		
50:50		
60:40		
80:20		
100:0		

The good morphology films were obtained according to the increasing average molecular weight of chitosan because of excellent cross-linking between polybenzoxazine and chitosan, strongly agree with the result reported by Zunying Liu and coworker. [15]

SEM micrographs show that the prepared polybenzoxazine/chitosan films were different morphology due to the polymer ratio. The surface of polybenzoxazine film and both chitosan films were dense and without any voids compared to polybenzoxazine/chitosan with variation ratio. There were many defects in 1.5CTS:PBZ-TETA, 20:80 film due to imperfect in cross-linking and rapidly evaporated solvent. When the chitosan ratio was increase, the better morphology of film surface was obtained. However, over 50 mole ratio of chitosan showed many flaws on the surface because of phase separation in polymer (Figure 1). This problem also present in polybenzoxazine/chitosan (Mw=100000 g/mol) films as shown in figure 2. The effect of phase separation was decreased with increasing the mole ratio of chitosan. It can be concluded that the average molecular weight and mole ratio of chitosan affected the morphology of cross-linking films. [15]

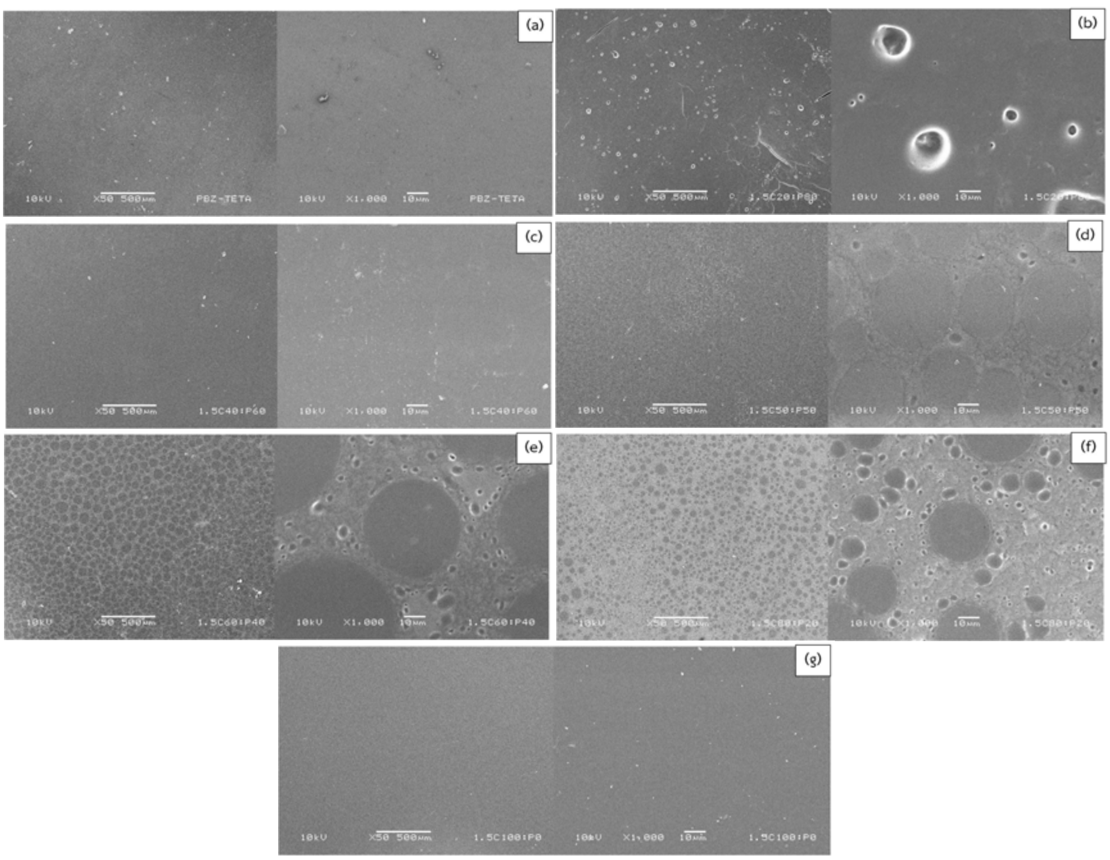

Figure 1 SEM micrographs of surface polybenzoxazine/chitosan (1.5CTS:PBZ-TETA) films with 0:100 (a), 20:80 (b), 40:60 (c), 50:50 (d), 60:40 (e), 80:20 (f), 100:0 (g).

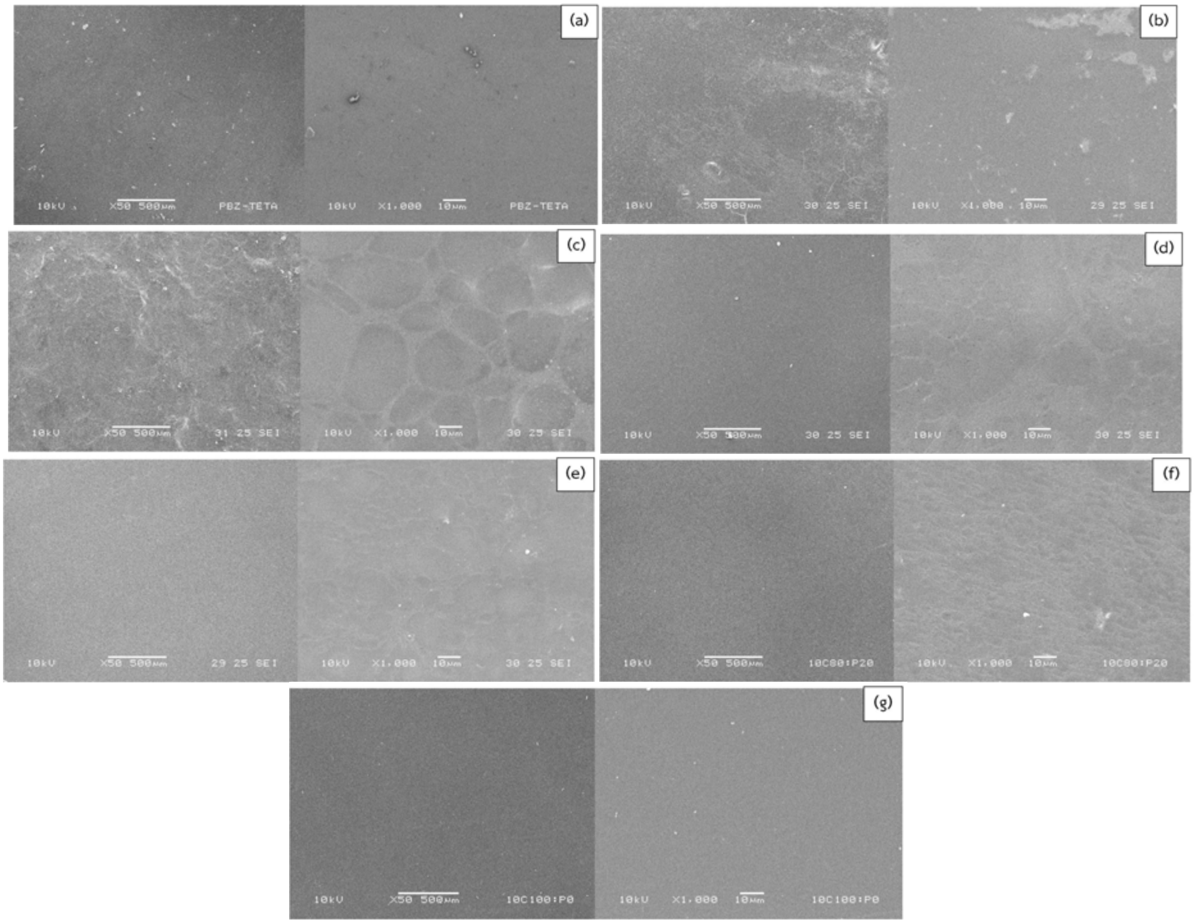

Figure 2 SEM micrographs of surface polybenzoxazine/chitosan (10CTS:PBZ-TETA) films with 0:100 (a), 20:80 (b), 40:60 (c), 50:50 (d), 60:40 (e), 80:20 (f), 100:0 (g).

Thermal Analysis

The polybenzoxazine/chitosan cross-linking films were studied thermal properties by using Thermogravimetric Analysis, TGA. The degradation of films began to degrade at 50 °C and the char yield was 10-28% as shown in Figure 3. Polybenzoxazine film had high initial thermal decomposition temperature, and its decomposition temperature spanned a wide range. The 5% weight-loss temperatures of the cross-linked films were between those of polybenzoxazine and chitosan. The char yield and initial thermal decomposition of our films was changed due to the mole ratio of polybenzoxazineand chitosan. Increasing polybenzoxazine mole ratio, the char yields were decrease excluding 10CTS:PBZ-TETA (50:50) char yield appeared higher %weight than chitosan film andpolybenzoxazine film, which indicated that the thermal stability of cross-linked film was improved. Thus the average molecular weight of chitosan had an effect on thermal stability due to the longer chain length. Moreover, the completely cross-linking between polybenzoxazine and chitosan was also affected thermal property. [16-18] These results indicate that the best mole ratio to prepare cross-linked film with good thermal property was 10CTS:PBZ-TETA (50:50).

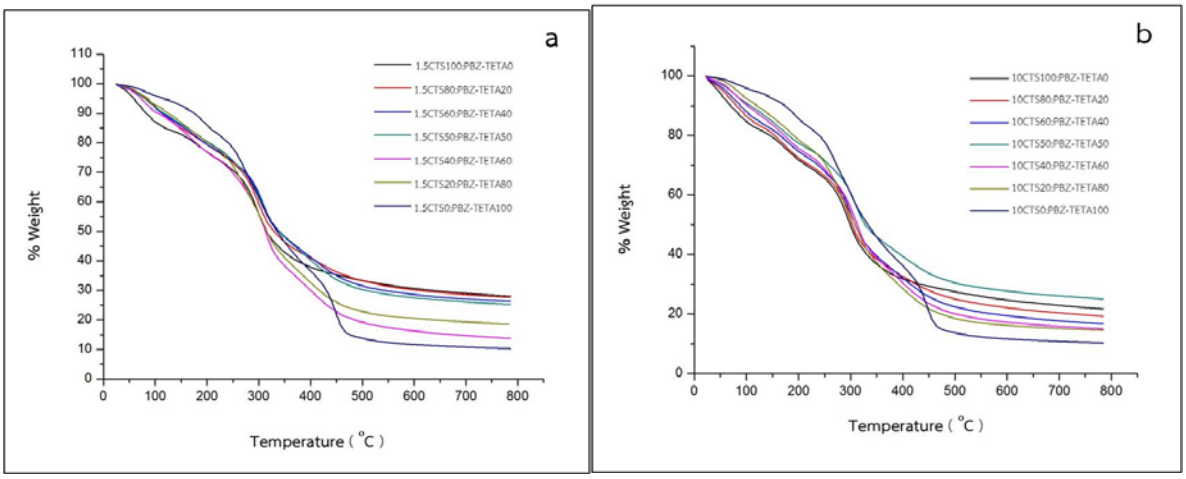

Figure 3 Thermogravimetric curves of polybenzoxazine/chitosan films, a: CTS (Mw=15000 g/mol), b: CTS (Mw=100000 g/mol)

Mechanical Analysis

The mechanical properties of the polybenzoxazine/chitosan films were investigated using uniaxial tensile test (Table 2). The Young's modulus of cross-linked films was lower than that of polybenzoxazine film and chitosan films; furthermore Young's modulus of cross-linked films was decrease with raising mole ratio of polybenzoxazine. The stress at break of cross-linked films was reduced according to increase the amount of polybenzoxazine in cross-linked film. Additionally, the %elongation at break was studied to explain the flexibility of cross-linked film, a higher elongation at break indicates greater flexibility. With low mole ratio of polybenzoxazine, the %elongation at break was decrease compared to polybenzoxazine film and chitosan film, and then it was slightly increase with reducing mole ratio of chitosan. 1.5CTS40:PBZ-TETA60 film showed higher %elongation at break than that of neat polymer films because of suitable mole ratio of good cross-linked ability of polybenzoxazineand chitosan. As a result of %elongation at break of polybenzoxazine/chitosan (Mw=100000) films, the results showed better flexibility than polybenzoxazine film, chitosan film and polybenzoxazine/chitosan (Mw=15000 g/mol) films. The most flexible film was 10CTS50:PBZ-TETA50 ratio which was 82.42 %elongation at break induced by the interactions between chitosan and polybenzoxazine.[19]

Conclusions

Polybenzoxazine/chitosan croos-linked films were successful to prepare with various mole ratio (polybenzoxazine:chitosan, 100:0, 80:20, 60:40, 50:50, 40:60, 20:80, 0:100). The combination between polybenzoxazine and chitosan with different average molecular weight (Mw=15000 g/mol and Mw=100000 g/mol) developed the properties of films compared to polybenzoxazine film and chitosan film. With high average molecular weight of chitosan, the films were performed flawlessly surface morphology.

Table 2 Tensile properties of polybenzoxazine/chitosan films

Mole ratio of films	Young's modulus (MPa)	stress at break (MPa)	% elongation at break
1.5CTS100:PBZ-TETA0	1007.02	21.56	20.02
1.5CTS80:PBZ-TETA20	933.34	37.61	3.53
1.5CTS60:PBZ-TETA40	580.38	20.64	6.19
1.5CTS50:PBZ-TETA50	400.75	12.57	6.59
1.5CTS40:PBZ-TETA60	229.26	2.75	43.57
1.5CTS20:PBZ-TETA80	nd*	nd*	nd*
1.5CTS0:PBZ-TETA100	1008.35	17.01	11.22
10CTS100:PBZ-TETA0	901.97	39.07	25.36
10CTS80:PBZ-TETA20	658.47	23.79	41.67
10CTS60:PBZ-TETA40	323.93	12.08	66.88
10CTS50:PBZ-TETA50	240.04	6.64	82.42
10CTS40:PBZ-TETA60	145.35	5.97	40.36
10CTS20:PBZ-TETA80	112.32	0.56	27.77
10CTS0:PBZ-TETA100	1008.35	17.01	11.22

*nd (not determined)

The thermal property of cross-linked films was improved by blending polybenzoxazine and chitosan (Mw=100000 g/mol) at 50:50 mole ratio which showed the highest char yield. Moreover, this mole ratio of polybenzoxazine in chitosan films also showed a significant role in enhancing the flexibility of cross-linked film.

Adcknowledgements

This research work is financially supported by Faculty of Science, Mahasarakham University; Biodegradable Polymers Research Unit, Faculty of Science, Mahasarakham University and, the Development and Promotion of Science and Technology Talents project (DPST).

References

1. Singh A, Narvi SS, Dutta PK, D Pandey N. External stimuli response on a novel chitosan hydrogel crosslinked with formaldehyde. Bulletin of Materials Science. 2006;29(3):233-8.
2. Roussy J, Chastellan P, van Vooren M, Guibal E. Treatment of ink-containing wastewater by coagulation/flocculation using biopolymers. Water Sa. 2005;31(3):369-76.
3. Jin J, Song M, Hourston DJ. Novel chitosan-based films cross-linked by genipin with improved physical properties. Biomacromolecules. 2004;5(1):162-8.
4. Grande R, Carvalho AJF. Compatible Ternary Blends of Chitosan/poly(vinyl alcohol)/poly(lactic acid) Produced by Oil-in-Water Emulsion Processing.

Biomacromolecules. 2011;12(4):907-14.

5. Ishida, H., Agag, T. Handbook of Benzoxazine Resins.Amsterdam: Elsevier; 2011. P.3-81.
6. Nair CPR. Advances in addition-cure phenolic resins. Progress in Polymer Science. 2004;29(5):401-98.
7. Ghosh NN, Kiskan B, Yagci Y. Polybenzoxazines - New high performance thermosetting resins: Synthesis and properties. Progress in Polymer Science. 2007;32(11):1344-91.
8. Takeich T, Agag T. High performance polybenzoxazines as novel thermosets. High Performance Polymers. 2006;18(5):777-97.
9. Sawaryn C, Landfester K, Taden A. Cationic Polybenzoxazines. A Novel Polyelectrolyte Class with Adjustable Solubility and Unique Hydrogen-Bonding Capabilities. Macromolecules. 2011;44(19):7668-74.
10. Holly FW, Cope AC, Condensation Products of Aldehydes and Ketones with o-Aminobenzyl Alcohol and o-Hydroxybenzylamine. Journal of the American Chemical Society. 1944;66:1875–1879.
11. Ning X, Ishida H, Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers. Journal of Polymer Science Part A: Polymer Chemistry. 1994;32(6):1121-1129.
12. Yagci Y, Kiskan B, Ghosh NN. Recent Advancement on Polybenzoxazine-A Newly Developed High Performance Thermoset. Journal of Polymer Science Part a-Polymer Chemistry. 2009;47(21):5565-76.
13. Lorjai P, Chaisuwan T, Wongkasemjit S. Porous structure of polybenzoxazine-based organic aerogel prepared by sol-gel process and their carbon aerogels. Journal of Sol-Gel Science and Technology. 2009;52(1):56-64.
14. Pakkethati K, Boonmalert A, Chaisuwan T, Wongkasemjit S. Development of polybenzoxazine membranes for ethanol-water separation via pervaporation. Desalination. 2011;267(1):73-81.
15. Liu Z, Ge X, Lu Y, Dong S, Zhao Y, Zeng M. Effects of chitosan molecular weight and degree of deacetylation on the properties of gelatine-based films. Food Hydrocolloids. 2012;26(1):311-7.
16. Demir KD, Kiskan B, Yagci Y. Thermally Curable Acetylene-Containing Main-Chain Benzoxazine Polymers via Sonogashira Coupling Reaction. Macromolecules. 2011;44(7):1801-7.
17. Rajput AB, Ghosh NN. Preparation and Characterization of Novel Polybenzoxazine-Polyester Resin Blends. International Journal of Polymeric Materials. 2011;60(1):27-39.
18. Li X, Xia Y, Xu W, Ran Q, Gu Y. The curing procedure for a benzoxazine-cyanate-epoxy system and the properties of the terpolymer. Polymer Chemistry. 2012;3(6):1629-33.
19. Leceta I, Guerrero P, de la Caba K. Functional properties of chitosan-based films. Carbohydrate Polymers. 2013;93(1):339-46.