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RESEARCH ARTICLE

Biodegradation behavior of two different chitosan films under controlled composting environment

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ABSTRACT

Chitosan has applications in different industries, due to the superior properties, causing an increase in the production of chitosan containing waste. Although composting is the most suitable method for biodegradable wastes like chitosan, less is known about the degradation of chitosan within the composting environment. In this study, biodegradation behavior of bare chitosan films and neutralized chitosan films were investigated under controlled composting environment according to international standards. CO_2 emission data showed higher degradation rate of bare chitosan films compared with neutralized chitosan films, which was also supported by SEM images and digital photographs in addition to the TGA and FTIR results. It can be concluded that the biodegradation rate of chitosan films under the composting environment is highly related to the amount of glycerol present in the films and the extraction rate of glycerol from film structure.

Keywords: Biodegradation, biopolymer, chitosan, composting

1. INTRODUCTION

Recently, with increasing economic growth, rapidly growing population, with the alteration of the standard of living, the amount of solid waste is increasing along with the changes in its composition. A large part of the generated solid waste is plastics, generally petrochemical-derived synthetic polymers. The overuse of plastic products causes some difficulties in waste management since they are not biodegradable. So, such wastes cause pollution of soil, groundwater and surface water resources. For this reason, the use of biodegradable polymers for various applications has become widespread. Chitosan is one of the most important biopolymers, which is deacetylated form of chitin, has applications in various fields such as medical, food and chemical industries due to mainly its biocompatible, biodegradable, antimicrobial, and nontoxic properties [1]. The form of the chitosan-based products in these areas can be diversified membranes, gels, films and hydrogels related to the intended purpose. The film is the preferred form of chitosan, incorporating with or without other polymers, essential oils, etc., in different areas like chemical engineering, medical, biotechnology, especially in the food industry as a packaging material [2-5]. Chitosan-based films have selective permeability to gases besides to non-toxic, biodegradable and antimicrobial nature thus they have great potential as a packaging material to extend of food shelf life [6-9]. For this reason usage of chitosan films will increase and in the meanwhile requirement to dispose of chitosan containing waste also.

Composting is a decomposition process of organic materials into stable humus that can be used to improve soil fertility [10, 11]. Composting is a suitable method for the disposal of biodegradable organic waste like chitosan containing wastes providing not only environmental benefits but also economic benefits [12]. There are only a few studies about biodegradation of chitosan in soil and the composting environment in the literature. Dean et al. [13] have reported that addition of nanoclay to chitosan films

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had no significant effect on degradation both in soil and composting conditions, which was prepared using melt processing method with or without glycerol as a plasticizer. Another study by Xie et al. [14] which has reported that the addition of glycerol and unmodified nanoclay caused to increase of biodegradation degree, mainly related to the addition of unmodified nanoclay. As a consequence, the chitosan biodegradation mechanism in a composting environment is not well defined yet. Therefore, we aimed to contribute to the studies related to the understanding of the biodegradation of chitosan in the composting environment by investigating the effect of neutralization of chitosan films since it was reported that neutralized films have no antimicrobial activity [4].

In this study, the effect of the neutralization process on biodegradation behavior of chitosan films, under controlled composting environment was investigated. Biodegradation of chitosan films, obtained with and without neutralization process, were investigated under controlled composting conditions according to international standards. In order to compare biodegradation behaviors of bare chitosan and neutralized chitosan films within composting environment, the amount of emitted CO_2, proof of the biodegradation by microbial activity, was evaluated in addition to characterization studies performed by FTIR, TGA, and SEM.

2. MATERIALS & METHOD

2.1. Preparation of films

Chitosan films were produced by the solvent casting method. Acetic acid (Sigma Aldrich) was used as a solvent and glycerol (Glycerol solution 84-88%, Sigma Aldrich) as a plasticizer. A 1% (w/v) chitosan (low molecular weight, with degree of deacetylation 75-85%, Sigma Aldrich) film solution was prepared with 1% (v/v) acetic acid solution [15]. After totally dissolving chitosan, glycerol was added at 0.2% (v/v). Solutions were filtered and then poured into petri dishes followed by drying of films at room temperature. After drying, for neutralization of chitosan films, the films were kept in 0.1 M NaOH solution for 30 minutes and then washed with distilled water and re-dried [16].

2.2. Composting system and biodegradation analysis

Biodegradation of films was investigated by measuring CO_2 emissions from composting reactors according to ASTM D-5338 and ISO 14855: 1, 2012 standards [17, 18]. Among the six parallel composting reactors used, two reactors were containing bare chitosan films, two were containing neutralized chitosan films while the remaining two were used as positive and negative controls containing cellulose and polyethylene films, respectively. Reactors were designed to incorporate 180 g total dry solids of compost and 30 g total dry solids of films according to the compost to polymer ratio given in the ASTM D-5338 and ISO 14855: 1, 2012 standards. Before biodegradation analysis, the films were cut to obtain a size of 1.5 cm x 1.5 cm of each piece of films. Mature compost was taken from a commercial composting plant that processes municipal solid wastes to high quality compost via tunnel composting system.

To obtain aerobic conditions, the air system was designed to send compressed air that provides CO_2-free, H_2O saturated air to each of the reactors at a sufficient airflow rate. Each reactor's air flow rate was regulated with a volumetric gas flow meter. Reactors were mixed periodically to obtain homogenous content. The temperature of the reactors was maintained at 58±2°C according to standards. During the process, moisture content was maintained over 50%. pH was measured throughout the process and digital photographs were taken at different time periods. The amount of CO_2, emitted as a biodegradation product, was measured by an infrared CO_2 analyzer (Model 902P O_2/CO_2 Analyzer, Quantek Instruments, USA).

2.3. SEM

Film samples were collected during the biodegradation process, rinsed with distilled water, air-dried, and coated with gold for sample imaging. Images of samples were obtained by scanning electron microscopy (SEM) using Nova™ NanoSEM 430 (FEI Company, USA).

2.4. FTIR

Fourier transform infrared (FTIR) spectra were measured on FTIR spectrophotometry (Nicolet 6700, Thermo Scientific) in the range of 4000 to 400 cm^{-1} for bare chitosan and neutralized chitosan films.

2.5. Thermal analysis

Thermal properties of the bare chitosan and neutralized chitosan films were investigated by thermogravimetric analysis (TGA) using TGA SII Exstar 6000 TG/DTA 6300. TGA was performed under a nitrogen atmosphere (10 mL min^{-1}) and film samples were heated to 600°C at a rate of 10°C min^{-1}.

3. RESULTS & DISCUSSION

In order to compare biodegradation behavior of bare and neutralized chitosan films digital photographs and SEM images, FTIR spectra and TGA thermograms of samples and carbon dioxide emission data were given below.

3.1. Digital photographs and SEM images

SEM images and digital photographs of bare chitosan film samples collected during the degradation process at different time periods are given in Fig 1. SEM images of bare chitosan films showed that the films had a homogeneous structure before degradation. After 5 days of biodegradation regular structure of film surfaces started to change. At the end of the first week, films were highly degraded, so it was not possible to take of bare chitosan film samples after 7 days. Different days were selected depending on the maximum CO_2 emissions for bare chitosan films. Size of films decreased during biodegradation as observed by digital photographs and by SEM images.

SEM images and digital photographs of neutralized chitosan film samples collected at different times of biodegradation are given in Fig 2. For neutralized chitosan films, same days were selected to compare the results with bare chitosan films. Digital photographs of neutralized chitosan films showed that the films were retained their structure for a long time when compared with bare chitosan films. Therefore, sampling from the reactors containing neutralized chitosan films was able to be continued to the end of the composting process. Correspondingly, the results of SEM analysis showed that at the end of the biodegradation process only a small amount of degradation has occurred.

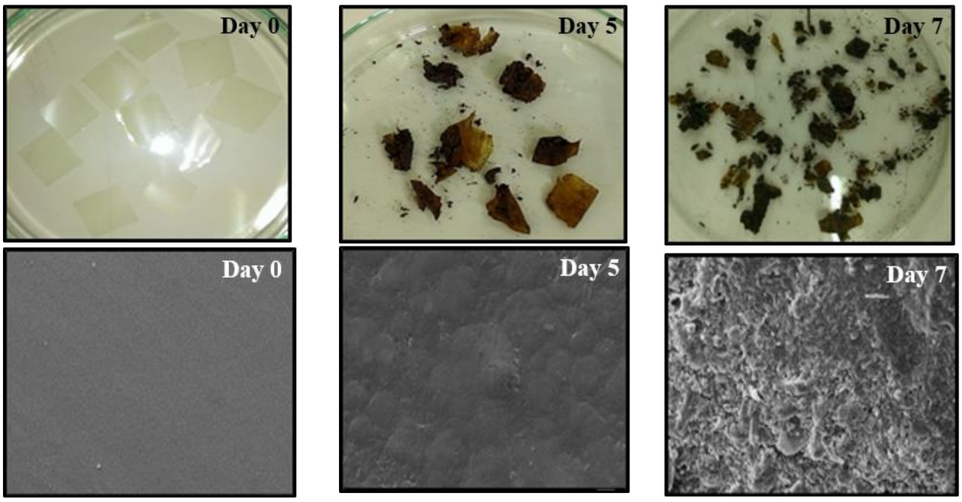

Fig 1. Digital photographs and SEM images of bare chitosan film samples

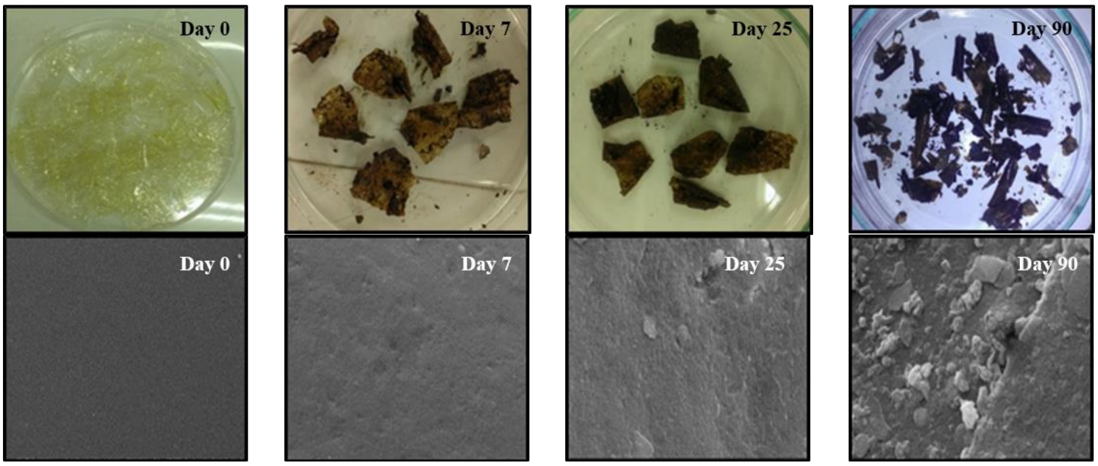

Fig 2. Digital photographs and SEM images of neutralized chitosan film samples

3.2. FTIR spectra

The absorption bands (1160-1140 cm^{-1}) corresponding to the FTIR spectra of C-O-C bond between the glucosidic units were used to represent the degradation of films due to microbial activity [19]. The decrease in intensity of the peak at 1150 cm^{-1} for bare chitosan films was attributed to the biodegradation of films by microbial activity (Fig 3, a and b). The intensity of the peak was not changed for neutralized chitosan films so it can be concluded that the films were not degraded by microorganisms (Fig 3, c and d).

3.3. Thermal Analysis

TGA of bare chitosan films and neutralized chitosan films that were collected before and after biodegradation process was carried out. Before degradation, weight loss was observed in three regions as 0-100°C, 150-200°C and 250-300°C for bare chitosan film samples corresponding to moisture loss, evaporation of glycerol [20] and degradation of chitosan respectively (Fig 4). Results of TG analysis emphasized that the degradation of chitosan films pursues upon glycerol molecules because the peak that corresponds to the evaporation of glycerol was disappeared for the samples of bare chitosan films after degradation. Meanwhile, there were only two peaks for neutralized films and the third peak corresponding to the evaporation of glycerol was already absent before degradation. Therefore, limited degradation could only be observed due to the lack of glycerol within the neutralized samples. Supporting these findings, it has been previously reported that using glycerol as a plasticizer makes films more hydrophilic and increase the biodegradation rate of films by microbial activity [21, 22]. Xie et al. [14] have reported that plasticized chitosan-based nano-biocomposites degraded more easily than unplasticized chitosan due to the presence of glycerol.

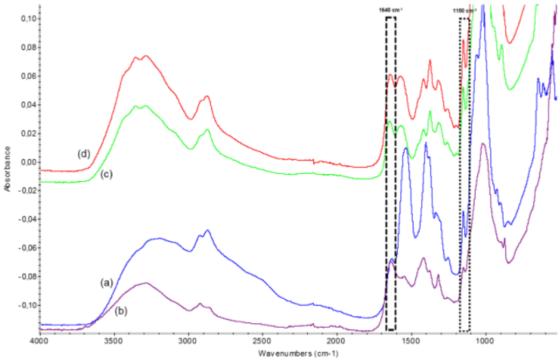

Fig 3. FTIR spectra of bare chitosan films (a) before and (b) after the degradation process; neutralized chitosan films (c) before and (d) after degradation process

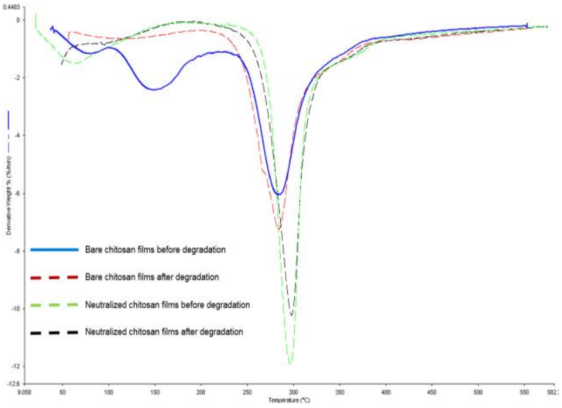

Fig 4. TGA thermograms of bare chitosan films and neutralized chitosan films before and after degradation

3.4. CO_2 Emissions

CO_2 emission data given in Fig 5 showed a high degradation rate of bare chitosan films compared with neutralized chitosan films especially during the first week of the process supporting the result given above. The probable reason for the lack of biodegradability after neutralization could be the elimination of glycerol during the neutralization step, the presence of which promotes microbial degradation. Therefore it can be concluded that the presence of glycerol is so dominant in biodegradability of chitosan films that the effect of the change in antimicrobial properties couldn't even be recognized in which case reverse data would be expected. Plasticization with glycerol makes films easily accessible for the microbial attack through the increase of water vapor permeability. The amount of carbon available to be metabolized to CO_2 in neutralized films would be less hence it is reasonable to observe less carbon dioxide emission from neutralized films containing reactor. But being even smaller than that of the negative control reactor may not be related only to the lack of glycerol. Microorganisms in the composting environment are mainly responsible for the biodegradation process of organic materials. Therefore it is reasonable to identify the microbial diversity, which has a major role in the degradation process. Further research is needed to understand the role of microorganisms and enzymes in the biodegradation of chitosan in the composting environment.

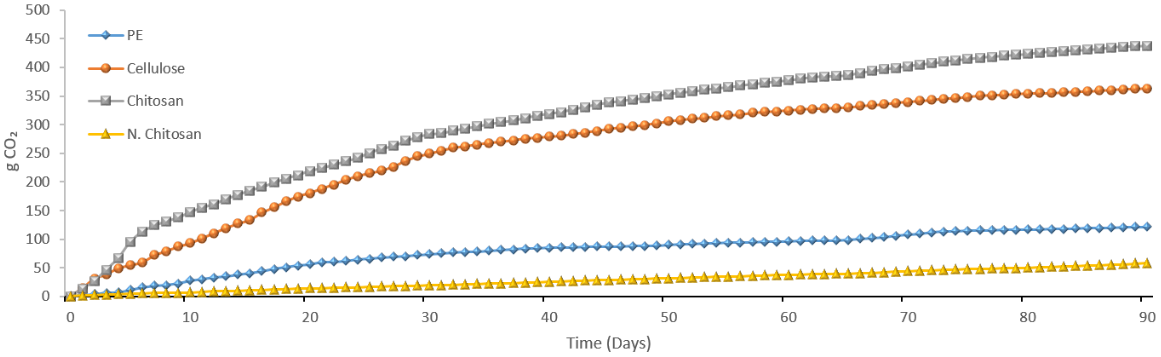

Fig 5. Cumulative CO_2 values (per vessel)

4. CONCLUSIONS

It was observed that the biodegradation rate of bare chitosan films is higher than that of neutralized chitosan films. Therefore, it can be concluded that the biodegradation rate of chitosan films under the composting environment is highly related to the amount of glycerol present in the films, and the extraction rate of glycerol from film structure but not the antimicrobial properties at all. Further research is needed to identify the microbial diversity, enzymes, plasticizer amount and film synthesizing techniques that play a role in the degradation process in order to increase the biodegradation rate of chitosan in the composting environment.

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REFERENCES

[1]. S.-H. Lim, and S.M. Hudson, "Review of Chitosan and Its Derivatives as Antimicrobial Agents and Their Uses as Textile Chemicals," Journal of Macromolecular Science Polymer Reviews, Vol. 43(2), p. 223-269, 2003.

[2]. M., Guo, T.Z. Jin, L. Wang, O.J. Scullen and C.H. Sommers "Antimicrobial films and coatings for inactivation of Listeria innocua on ready-to-eat deli turkey meat," Food Control, Vol. 40, pp. 64-70, 2014.

[3]. D.E. Altiok and F. Tihminlioglu, "Physical, antibacterial and antioxidant properties of chitosan films incorporated with thyme oil for potential wound healing applications," Journal of Materials Science Materials in Medicine, Vol. 21(7), pp. 2227-2236, 2010.

[4]. P. Fernandez-Saiz, J.M. Lagaron and M.J. Ocio, "Optimization of the biocide properties of chitosan for its application in the design of active films of interest in the food area," Food Hydrocolloids, Vol. 23(3), pp. 913-921, 2009.

[5]. T. Freier, H.S. Koh, K. Kazazian and M.S. Shoichet, "Controlling cell adhesion and degradation of chitosan films by N-acetylation," Biomaterials, Vol. 26(29), pp. 5872-8 2005.

[6]. J. Bonilla, E. Fortunati, L. Atarés, A. Chiralt and J.M. Kenny, "Physical, structural and antimicrobial properties of poly vinyl alcohol–chitosan biodegradable films," Food Hydrocolloids, Vol. 35, pp. 463-470, 2014.

[7]. P. Fernández-Saiz, G. Sánchez, C. Soler and J.M. Lagaron, "Chitosan films for the microbiological preservation of refrigerated sole and hake fillets," Food Control, Vol. 34(1), pp. 61-68, 2013.

[8]. Q. Ma, Y. Zhang, F. Critzer, P.M. Davidson, S. Zivanovic and Q. Zhong, "Physical, mechanical, and antimicrobial properties of chitosan films with microemulsions of cinnamon bark oil and soybean oil," Food Hydrocolloids, Vol. 52, pp. 533-542, 2016.

[9]. Z.H. Zhang, Z. Han, X.A. Zeng, X.Y. Xiong and Y.J. Liu, "Enhancing mechanical properties of chitosan films via modification with vanillin," International Journal of Biological Macromolecules, Vol. 81, pp. 638-43, 2015.

[10]. C.M. Mehta, U. Palni, I.H. Franke-Whittle and A.K. Sharma, "Compost Its role, mechanism and impact on reducing soil-borne plant," Waste Management, Vol. 34, pp. 607-622, 2014.

[11]. P.M. Dees and W.C. Ghiorse, "Microbial diversity in hot synthetic compost as revealed by PCR-amplified rRNA sequences from cultivated isolates and extracted DNA," FEMS Microbiology Ecology, Vol. 35, pp. 207-216, 2001.

[12]. I. Leceta, P. Guerrero, S. Cabezudo and K. de la Caba, "Environmental assessment of chitosan-based films," Journal of Cleaner Production, Vol. 41, pp. 312-318, 2013.

[13]. K. Dean, P. Sangwan, C. Way, X. Zhang, V.P. Martino, F. Xie, P.J. Halley, E. Pollet and L. Avérous, "Glycerol plasticised chitosan: A study of biodegradation via carbon dioxide evolution and nuclear magnetic resonance," Polymer Degradation Stability, Vol. 98(6), pp. 1236-1246, 2013.

[14]. D.F. Xie, V.P. Martino, P. Sangwan, C. Way, G.A. Cash, E. Pollet, K.M. Dean, P.J. Halley and L. Avérous, "Elaboration and properties of plasticised chitosan-based exfoliated nano-biocomposites," *Polymer*, Vol. 54(14), p. 3654-3662, 2013.

[15]. I. Leceta, P. Guerrero, and K. de la Caba, "Functional properties of chitosan-based films," *Carbohydrate Polymers*, Vol. 93(1), pp. 339-46, 2013.

[16]. A.P. Martínez-Camacho, M.O. Cortez-Rocha, J.M. Ezquerra-Brauer, A.Z. Graciano-Verdugo, F. Rodriguez-Félixa, M.M. Castillo-Ortega, M.S. Yépiz-Gómez and M. Plascencia-Jatomea, "Chitosan composite films: Thermal, structural, mechanical and antifungal properties," *Carbohydrate Polymers*, Vol. 82(2), pp. 305-315, 2010.

[17]. D5338-98 American Society for Testing Materials (ASTM), Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions. ASTM International, West Conshocken, PA, 2003.

[18]. EN ISO 14855-1, Determination of the Ultimate Aerobic Biodegradability and Disintegration of Plastic Materials under Controlled Composting Conditions—Method by Analysis of Evolved Carbon dioxide-Part 1: General method. 2012.

[19]. M. Kammoun, M. Haddar, T.K. Kallel, M. Dammak and A. Sayari "Biological properties and biodegradation studies of chitosan biofilms plasticized with PEG and glycerol," *International Journal of Biological Macromolecules*, Vol. 62, pp. 433-8, 2013.

[20]. M. Kurek, C.H. Brachais, C.M. Nguimjeu, A. Bonnotte, A. Voilley, K. Galić, J.-P. Couvercelle and F. Debeaufort, "Structure and thermal properties of a chitosan coated polyethylene bilayer film," Polymer Degradation and Stability, Vol. 97(8), pp. 1232-1240, 2012.

[21]. R. Lamim, R.A. de Freitas, E.I. Rudek, H.M. Wilhelm, O.A. Cavalcanti and T.M.B. Bresolin, "Films of chitosan andN-carboxymethylchitosan. Part II: effect of plasticizers on their physiochemical properties," *Polymer International,* Vol. 55(8), pp. 970-977, 2006.

[22]. N. Suyatma, L. Tighzert and A. Copinet, "Effects of hydrophilic plasticizers on mechanical, thermal, and surface properties of chitosan films," *Journal of Agricultural and Food Chemistry*, Vol. 53, pp. 3950-3957, 2005.