



# Polymer Degradation and Stability

ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

Journal Pre-proof

Contents lists available at ScienceDirect

**Polymer Degradation and Stability**

Journal homepage: [www.elsevier.com/locate/polystab](http://www.elsevier.com/locate/polystab)

**Degradation of chitosan by sonication in very-low-concentration acetic acid**

Emma Savitri<sup>a</sup>, Sri Rachmanita Juliasruti<sup>a</sup>, Amarakulmi Haraharati<sup>a</sup>, Sumarno, Achmad Roesyad<sup>b</sup>

<sup>a</sup> Institut Teknologi Sepuluh Nopember, Indonesia; <sup>b</sup> Institut Teknologi Sepuluh Nopember, Indonesia

**ARTICLE INFO**

Article history:  
Received 13 April 2014  
Received in revised form 10 September 2014  
Accepted 14 September 2014  
Available online 2 October 2014

**Keywords:**  
Chitosan  
Sonication  
Molecular weight  
Degree of substitution

**ABSTRACT**

Chitosan, a linear polysaccharide consisting of 1,4- and 1,6-linked 2-deoxy-2-amino-2,3,6-tri-O-acetyl-D-glucan (D-GlcNAc) and 2-amino-2-deoxy-D-glucan (2-D-Glc) units in varying proportions, having a high molecular weight and (1→6) and (1→3) linkages, has become an alternative for degrading chitosan into low molecular weight (LMW) chitosan fragments and monomers. In this study, chitosan was treated with ultrasonic at 40, 60, 80, and 100 min with various acetic acid concentrations (0.25 wt%, 1 wt%, 5 wt%, and 10 wt%) and sonication frequencies as a solvent and without other reagents. The findings were used to study the changes in molecular weight, zero-order degradation of chitosan, hydroxylation and glycosylation degree of chitosan, degree of acetylation, degree of epitylation, and monomer. The results are as follows: in the first study, two mechanisms of (1→3) and (1→6) linkage cleavage were observed. The maximum cleavage efficiency was observed with concentration 0.25 wt% acetic acid and 40 min sonication. The cleavage efficiency of chitosan was 24.72, 20.76, and 43.64 wt%, respectively. However, a maximum decrease in molecular weight was 77.72, 93.18, 91.38, and 91.06%, respectively. The results of hydroxylation and glycosylation of the degraded chitosan, but not change in molecular weight, the results had a tendency to increase. The degree of hydroxylation increased to 60.00 wt% of the glucose unit by 2014 Elsevier Ltd. All rights reserved.

**1. Introduction**

Chitosan is a linear copolymer consisting of 1,4- and 1,6-linked 2-acetyl-2-amino-2,3,6-tri-O-acetyl-D-glucan (D-GlcNAc) and 2-amino-2-deoxy-D-glucan (D-Glc) units in varying proportions. It is the most important derivative of chitin, a member of nitrogen-containing saccharide low molecular weight chitosan (LMWC) chitosan derivatives (CDs) and has various uses, high potential for biomedical and pharmaceutical applications, especially CDs, that has uses as drugs for adjuvant [1–3], anti-tumoral agents [4], as substances at wound dressing [5], as vectors in gene therapy [6,7], and as glucose-binding and chelating [10–14].

A number of different degradation methods, such as chemical hydrolysis [15,16], redox reaction degradation [18–21], and enzymatic treatments [22] were reported. In particular, low molecular weight chitosan (LMWC) and chitosan oligomers (COs). Chemical hydrolysis uses both strong and weak acids as hydrolysis agents to obtain glucosamine and oligosaccharides containing high concentrations of acetyl has some environmental issues, but produces high yields of small fragments and high rates of chitosan hydrolysis. Furthermore, an excess acid treatment results in the degradation of glucosamine, which significantly reduces the yield [18–21]. The enzymatic process generally takes place under mild conditions but the reaction rate is slow. Furthermore, the enzyme prices are high and the enzymes are not easily controlled [22–24].

Oxidative degradation by consecutive nitrous acid peroxides on chitosan with 0.25 wt% acetic acid units and the end products (containing 2,3,6-tri-O-acetyl-D-glucosamine) by ultrasonic [11].

The utilization of very low concentration of weak acids combined with sonication might provide an alternative method to strong acid hydrolysis, even though the degradation rates for one soluble chitosan and for the weak acid limit and soluble fractions in a solvent. The concentration used was initially 0.1 wt% [15], whereas 1–20 wt% concentration were also evaluated [26–32]. Below this limit, chitosan will not only partially give rise to CD, but also at pH the acid provides the H<sup>+</sup> that will promote the amino groups of chitosan. In this study, the hydrolysis was carried out under the condition of acidic groups available in aqueous devices.

Corresponding author. Tel.: +62 31 7494111; fax: +62 31 7494111.  
E-mail addresses: [emma.savitri@itb.ac.id](mailto:emma.savitri@itb.ac.id), [achmadr@itb.ac.id](mailto:achmadr@itb.ac.id) (A. Roesyad).

<http://dx.doi.org/10.1016/j.polystab.2014.09.004>

0141-3910/\$ – see front matter © 2014 Elsevier Ltd. All rights reserved.



## AIMS AND SCOPE

*Polymer Degradation and Stability* deals with the degradation reactions and their control which are a major preoccupation of practitioners of the many and diverse aspects of modern polymer technology.

Deteriorative reactions occur during processing, when polymers are subjected to heat, oxygen and mechanical stress, and during the useful life of the materials when oxygen and sunlight are the most important degradative agencies. In more specialised applications, degradation may be induced by high energy radiation, ozone, atmospheric pollutants, mechanical stress, biological action, hydrolysis and many other influences. The mechanisms of these reactions and stabilisation processes must be understood if the technology and applications of polymers are to continue to advance. The reporting of investigations of this kind is therefore a major function of this journal.

However there are also new developments in polymer technology in which degradation processes find positive applications. For example, photodegradable plastics are now available, the recycling of polymeric products will become increasingly important, degradation and combustion studies are involved in the definition of the fire hazards which are associated with polymeric materials and the microelectronics industry is vitally dependent upon polymer degradation in the manufacture of its circuitry. Polymer properties may also be improved by processes like curing and grafting, the chemistry of which can be closely related to that which causes physical deterioration in other circumstances.

Radiation of various kinds is used to initiate many of these modern technological processes so that polymer photochemistry has come to a new prominence and finds a major place in this journal.

The study of all these processes has made extensive use of modern instrumental analytical methods and the various spectrometric, chromatographic and thermal analysis techniques have been particularly prominent.

There is clearly a strong common bond between investigators in various parts of the field. *Polymer Degradation and Stability* provides a forum for the publication of their work.

### **Editor-in-Chief and Editor for General Degradation**

**J.-L. GARDETTE**

Université Blaise Pascal, Institut de Chimie de Clermont  
Ferrand, Equipe Photochimie, Campus des Cézeaux,  
63170 Aubièrre, France  
E-mail: luc.gardette.pds@univ-bpclermont.fr

### **Editor for General Degradation**

**G. A. GEORGE**

Queensland University of Technology,  
Brisbane, 4000, Australia  
E-mail: g.george@qut.edu.au

### **Editor for Biodegradable and Bio-based Polymers**

**T. IWATA**

Science of Polymeric Materials, Department of Biomaterial  
Sciences, Graduate School of Agricultural and Life  
Sciences, University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku,  
Tokyo 113-8657, Japan  
E-mail: atiwata@mail.ecc.u-tokyo.ac.jp

### **Editor for Fire Retardants and Nanocomposites**

**B. SCHARTEL**

BAM Federal Institute for Materials Research and Testing,  
Unter den Eichen 87, 12205 Berlin, Germany  
E-mail: bernhard.schartel@bam.de

**Honorary Editor-in-Chief: N. C. BILLINGHAM**

**Editor Emeritus: N. GRASSIE** (Founding Editor)

### **Editorial Board**

#### **H. Abe**

RIKEN Biomass Engineering Program,  
Wako, Japan

#### **A.-C. Albertsson**

The Royal Institute of Technology,  
Stockholm, Sweden

#### **N. S. Allen**

Chemistry Department, Manchester  
Metropolitan University, UK

#### **S. Al-Malaika**

Aston University, Birmingham, UK

#### **G. Camino**

Politecnico di Torino, Alessandria, Italy

#### **M. Celina**

Sandia National Laboratories,  
Albuquerque, NM, USA

#### **E. Chiellini**

University of Pisa, Italy

#### **Y. Doi**

The Institute of Physical and Chemical  
Research, Saitama, Japan

#### **P. Gijsman**

DSM Research, Geleen,  
The Netherlands

#### **S. S. Im**

Hanyang University, Seoul, Korea

#### **F. P. La Mantia**

Universita di Palermo, Italy

#### **H. Nishida**

Kyushu Institute of Technology,  
Kitakyushu, Japan

#### **J. Pickett**

Schenectady  
NY, USA

#### **J. Scheirs**

ExcelPlas Australia, Edithvale, VIC, Australia

#### **W. H. Starnes**

Department of Chemistry,  
College of William and Mary Williamsburg,  
Virginia, USA

#### **J. Wang**

National Flame Retardant Materials Laboratory,  
School of Chemical Engineering, Beijing  
Institute of Technology, Beijing, China

#### **C. A. Wilkie**

Department of Chemistry,  
Marquette University, Milwaukee, WI, USA

**Publication information:** *Polymer Degradation and Stability* (ISSN 0141-3910). For 2014, volumes 99-110 (12 issues) are scheduled for publication. Subscription prices are available upon request from the Publisher or from the Elsevier Customer Service Department nearest you or from this journal's website (<http://www.elsevier.com/locate/polydegstab>). Further information is available on this journal and other Elsevier products through Elsevier's website: (<http://www.elsevier.com>). Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by standard mail (surface within Europe, air delivery outside Europe). Delivery rates are available upon request. Claims for missing issues should be made within six months of the date

## Editorial Board

Enhanced polyimide proportion effects on fire behavior of isocyanate-based polyimide foams by refilled aromatic dianhydride method

Pages 1-12

Gaohui Sun, Lianhe Liu, Jun Wang, Hongliang Wang, Zhong Xie, Shihui Han

Polyurethane thermal effects studied using two-dimensional correlation infrared spectroscopy

Pages 13-22

Heliang Sui, Xueyong Liu, Fachun Zhong, Kemei Cheng, Yiwei Luo, Xin Ju

Shielding Kevlar fibers from atomic oxygen erosion via layer-by-layer assembly of nanocomposites

Pages 23-26

Xin Sui, Longcheng Gao, Penggang Yin

Synthesis and fire properties of rigid polyurethane foams made from a polyol derived from melamine and cardanol

Pages 27-34

Meng Zhang, Jinwen Zhang, Shuigen Chen, Yonghong Zhou

On the microstructure of polypropylenes by pyrolysis GC-MS

Pages 35-43

Maria Paola Luda, Riccardo Dall'Anese

Enzymatic characterization of a depolymerase from the isolated bacterium *Variovorax* sp. C34 that degrades poly(enriched lactate-co-3-hydroxybutyrate)

Pages 44-49

Jian Sun, Ken'ichiro Matsumoto, John Masani Nduko, Toshihiko Ooi, Seiichi Taguchi

Novel poly(xylitol sebacate)/hydroxyapatite bio-nanocomposites via one-step synthesis

Pages 50-55

Piming Ma, Ting Li, Wei Wu, Dongjian Shi, Fang Duan, Huiyu Bai, Weifu Dong, Mingqing Chen

Pros and cons of melt annealing on the properties of MWCNT/polypropylene composites

Pages 56-64

Gennaro Gentile, Veronica Ambrogi, Pierfrancesco Cerruti, Rosa Di Maio, Giuseppe Nasti, Cosimo Carfagna

Hydrolysis of poly(lactic acid) into calcium lactate using ionic liquid [Bmim][OAc] for chemical recycling

Pages 65-70

Xiuyan Song, Hui Wang, Xuequn Yang, Fusheng Liu, Shitao Yu, Shiwei Liu

Selective carboxylate induced thermal degradation of bacterial poly(3-hydroxybutyrate-co-4-hydroxybutyrate) – Source of linear uniform 3HB4HB oligomers

Pages 71-79

Michał Kwiecień, Michał Kawalec, Piotr Kurcok, Marek Kowalczyk, Grażyna Adamus

Modeling the pH-dependent PLA oligomer degradation kinetics

Pages 80-90

S. Lazzari, F. Codari, G. Storti, M. Morbidelli, D. Moscatelli

Synergistic effects of kaolin clay on intumescent fire retardant coating composition for fire protection of structural steel substrate

*Pages 91-103*

Sami Ullah, Faiz Ahmad, A.M. Shariff, M.A. Bustam

Synthesis of a hyperbranched poly(phosphamide ester) oligomer and its high-effective flame retardancy and accelerated nucleation effect in polylactide composites

*Pages 104-112*

Zhi Li, Ping Wei, Ying Yang, Yonggang Yan, Dean Shi

Effect of squalene absorption on oxidative stability of highly crosslinked UHMWPE stabilized with natural polyphenols

*Pages 113-120*

Jie Shen, Xincui Liu, Jun Fu

Hydrolytic degradation and bioactivity of lactide and caprolactone based sponge-like scaffolds loaded with bioactive glass particles

*Pages 121-128*

A. Larrañaga, P. Aldazabal, F.J. Martin, J.R. Sarasua

Stability of MEH-PPV: Poly[[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene]vinylene] in solutions exposed to air in the dark and at daylight at laboratory temperature

*Pages 129-136*

Dmitrij Bondarev, Olga Trhliková, Jan Sedláček, Jiří Vohlídal

Influence of exfoliated graphite nanoplatelets on the flammability and thermal properties of polyethylene terephthalate/polypropylene nanocomposites

*Pages 137-148*

I.M. Inuwa, Azman Hassan, De-Yi Wang, S.A. Samsudin, M.K. Mohamad Haafiz, S.L. Wong, M. Jawaid

Synthesis of Diels–Alder network polymers from bisfuranic terminated poly(L-lactide) and tris-maleimide

*Pages 149-155*

Kazuki Ishida, Yukiko Furuhashi, Naoko Yoshie

Degradation of poly(L-lactide) under KrF excimer laser treatment

*Pages 156-164*

Bogusz D. Stępak, Arkadiusz J. Antończak, Konrad Szustakiewicz, Paweł E. Koziół, Krzysztof M. Abramski

One-pot synthesis of a novel s-triazine-based hyperbranched charring foaming agent and its enhancement on flame retardancy and water resistance of polypropylene

*Pages 165-174*

Panyue Wen, Xiaofeng Wang, Bibo Wang, Bihe Yuan, Keqing Zhou, Lei Song, Yuan Hu, Richard K.K. Yuen

Influence of PE/PP ratio and ENB content on the degradation kinetics of  $\gamma$ -irradiated EPDM

*Pages 175-183*

A. De Almeida, L. Chazeau, G. Vigier, G. Marque, Y. Goutille

Physicochemical characterization of ethanol organosolv lignin (EOL) from *Eucalyptus globulus*: Effect of extraction conditions on the molecular structure

*Pages 184-194*

Mauricio Yáñez-S, Betty Matsuhira, Carolina Nuñez, Shaobo Pan, Christopher A. Hubbell, Poulomi Sannigrahi, Arthur J. Ragauskas

Ablation and thermo-mechanical investigation of short carbon fiber impregnated elastomeric ablatives for ultrahigh temperature applications

---

*Pages 195-202*

M. Bassyouni, Nadeem Iqbal, Sadia Sagar Iqbal, S.M.-S. Abdel-hamid, M.H. Abdel-Aziz, Umair Javaid, Mohammad Bilal Khan

Modeling of nonlinear viscoelasticity-viscoplasticity of bio-based polymer composites

*Pages 203-207*

E. Kontou, G. Spathis, P. Georgiopoulos

Thermal decomposition kinetics of balsa wood: Kinetics and degradation mechanisms comparison between dry and moisturized materials

*Pages 208-215*

Luan TranVan, Vincent Legrand, Frédéric Jacquemin

Effects of thermal aging on the water uptake behavior of pultruded BFRP plates

*Pages 216-224*

Zhongyu Lu, Guijun Xian, Hui Li

Temperature-dependent viscosity model of HPAM polymer through high-temperature reservoirs

*Pages 225-231*

ByungIn Choi, Moon Sik Jeong, Kun Sang Lee

Study of the stability of siloxane stone strengthening agents

*Pages 232-240*

Elena Tesser, Fabrizio Antonelli, Laura Sporni, Renzo Ganzerla, Noni-Pagona Maravelaki

Further progress into the thermal characterization of HCN polymers

*Pages 241-251*

José L. de la Fuente, Marta Ruiz-Bermejo, Delphine Nna-Mvondo, Robert D. Minard

Special Spherical Shell-shaped Foam deriving from Guanidine Phosphate – Pentaerythritol system and its Intumescent Fire Retardant effects on Polypropylene

*Pages 252-259*

Fangfang Jin, Yin Xia, Zongwen Mao, Yifei Ding, Yong Guan, Anna Zheng

Preparation of silica-supported 2-mercaptobenzimidazole and its antioxidative behavior in styrene-butadiene rubber

*Pages 260-267*

Bangchao Zhong, Qifeng Shi, Zhixin Jia, Yuanfang Luo, Yongjun Chen, Demin Jia

The flame-retardancy and anti-dripping properties of novel poly(ethylene terephthalate)/cyclotriphosphazene/silicone composites

*Pages 268-277*

Jiawei Li, Feng Pan, Hong Xu, Linping Zhang, Yi Zhong, Zhiping Mao

Mesophilic anaerobic biodegradation test and analysis of eubacteria and archaea involved in anaerobic biodegradation of four specified biodegradable polyesters

*Pages 278-283*

Hisaaki Yagi, Fumi Ninomiya, Masahiro Funabashi, Masao Kunioka

Lipase mediated enzymatic degradation of polydioxanone in solution

*Pages 284-289*

Aditi Banerjee, Kaushik Chatterjee, Giridhar Madras

The potential of metal oxalates as novel flame retardants and synergists for engineering polymers

*Pages 290-297*

A.F. Holdsworth, A.R. Horrocks, B.K. Kandola, D. Price

Photocurable polythiol based (meth)acrylate resins stabilization: New powerful stabilizers and stabilization systems

*Pages 298-307*

Zakaria Belbakra, Zoubair M. Cherkaoui, Xavier Allonas

Kinetics of radiation-induced degradation of CF<sub>2</sub>- and CF-groups in poly(vinylidene fluoride): Model refinement

*Pages 308-311*

Alena Leonidovna Sidelnikova, Vladimir Petrovich Andreichuk, Leonid Abramovich Pesin, Sergey Evgenievich Evsyukov, Igor Vasil'evich Gribov, Natalia Anatol'evna Moskvina, Vadim L'vovich Kuznetsov

Hydrolytic degradation of monomer casting nylon in subcritical water

*Pages 312-317*

Wei Wang, Linghui Meng, Yudong Huang

Reaction model describing antioxidant depletion in polyethylene–clay nanocomposites under thermal aging

*Pages 318-335*

Iftekhar Ahmad, Christopher Y. Li, Y. Grace Hsuan, Richard A. Cairncross

Macromolecular antioxidants via thiol-ene polyaddition and their synergistic effects

*Pages 336-343*

Stephan Beer, Ian Teasdale, Oliver Brueggemann

Degradation of chitosan by sonication in very-low-concentration acetic acid

*Pages 344-352*

Emma Savitri, Sri Rachmania Juliastuti, Anitarakhmi Handaratri, Sumarno, Achmad Roesyadi

Influence of melt processing conditions on poly(lactic acid) degradation: Molar mass distribution and crystallization

*Pages 353-363*

Pierre Erwan Le Marec, Laurent Ferry, Jean-Christophe Quantin, Jean-Charles Bénézet, Frédéric Bonfils, Stéphane Guilbert, Anne Bergeret

Cu- and Zn-acetate-containing ionic liquids as catalysts for the glycolysis of poly(ethylene terephthalate)

*Pages 364-377*

A.M. Al-Sabagh, F.Z. Yehia, A.M.F. Eissa, M.E. Moustafa, Gh. Eshaq, A.M. Rabie, A.E. ElMetwally

Study of the effect of atmospheric pressure air dielectric barrier discharge on nylon 6,6 foils

*Pages 378-388*

Anna Kuzminova, Artem Shelemin, Ondřej Kylián, Andrei Choukourov, Helena Valentová, Ivan Krakovský, Jan Nedbal, Danka Slavínská, Hynek Biederman

Free-volume hole size evaluated by positron annihilation lifetime spectroscopy in the amorphous part of poly(ethylene terephthalate) degraded by a weathering test

*Pages 389-394*

Hideaki Hagihara, Akihiro Oishi, Masahiro Funabashi, Masao Kunioka, Hiroyuki Suda

Catalytic pyrolysis and flame retardancy of epoxy resins with solid acid boron phosphate

*Pages 395-404*

You Zhou, Jie Feng, Hui Peng, Hongqiang Qu, Jianwei Hao

Reactive UV-absorber and epoxy functionalized soybean oil for enhanced UV-protection of clear coated wood

*Pages 405-414*

Sara K. Olsson, Mats Johansson, Mats Westin, Emma Östmark

A molecular based kinetic study on the thermal decomposition of poly- $\alpha$ -methyl styrene

*Pages 415-421*

Jia Fu, Weiguo Sun, Yonghong Jiang, Qunchao Fan, Yi Zhang, Zhanwen Zhang

Depth-resolved infrared microscopy and UV-VIS spectroscopy analysis of an artificially degraded polyester-urethane clearcoat

*Pages 422-434*

Koen N.S. Adema, Hesam Makki, Elias A.J.F. Peters, Jozua Laven, Leendert G.J. van der Ven, Rolf A.T.M. van Benthem, Gijsbertus de With

Studying the effect of the chloral group on the thermal and physical properties of aromatic cyanate esters

*Pages 435-446*

Ian Hamerton, Brendan J. Howlin, Lyndsey Mooring, Corinne Stone, Martin Swan, Scott Thompson

Disulfides – Effective radical generators for flame retardancy of polypropylene

*Pages 447-456*

Weronika Pawelec, Anton Holappa, Teija Tirri, Melanie Aubert, Holger Hoppe, Rudolf Pfaendner, Carl-Eric Wilén

Long term aging of LLDPE based multi-layer film by exposure to light hydrocarbons

*Pages 457-463*

Moshe Rabaev, Nir Goldin, Konstantin Tartakovsky, Itamar Tzadok, Udi Akiva, Roni Shneck, Moshe Gottlieb

Hygrothermal aging effects on fatigue of glass fiber/polydicyclopentadiene composites

*Pages 464-472*

Yinghui Hu, Augustus W. Lang, Xiaochen Li, Steven R. Nutt

*In vitro* degradation study of novel HEC/PVA/collagen nanofibrous scaffold for skin tissue engineering applications

*Pages 473-481*

Farah Hanani Zulkifli, Fathima Shahitha Jahir Hussain, Mohammad Syaiful Bahari Abdull Rasad, Mashitah Mohd Yusoff

Catalytic and thermal pyrolysis of polycarbonate in a fixed-bed reactor: The effect of catalysts on products yields and composition

*Pages 482-491*

E.V. Antonakou, K.G. Kalogiannis, S.D. Stefanidis, S.A. Karakoulia, K.S. Triantafyllidis, A.A. Lappas, D.S. Achilias

A statistical experimental design approach for photochemical degradation of aqueous polyacrylic acid using photo-Fenton-like process

*Pages 492-497*

Samira Ghafoori, Mehrab Mehrvar, Philip K. Chan

Analytical evaluation of the performance of stabilization systems for polyolefinic materials. Part I: Interactions between hindered amine light stabilizers and phenolic antioxidants

*Pages 498-508*

Susanne Beißmann, Michael Reisinger, Klemens Grabmayer, Gernot Wallner, David Nitsche, Wolfgang Buchberger

Analytical evaluation of the performance of stabilization systems for polyolefinic materials. Part II: Interactions between hindered amine light stabilizers and thiosynergists

*Pages 509-517*

Susanne Beißmann, Klemens Grabmayer, Gernot Wallner, David Nitsche, Wolfgang Buchberger

Forensic engineering of advanced polymeric materials – Part II: The effect of the solvent-free non-woven fabrics formation method on the release rate of lactic and glycolic acids from the tin-free poly(lactide-co-glycolide) nonwovens

*Pages 518-528*

Wanda Sikorska, Grazyna Adamus, Piotr Dobrzynski, Marcin Libera, Piotr Rychter, Izabella Krucinska, Agnieszka Komisarczyk, Mariana Cristea, Marek Kowalczuk

Crystallization behaviors of poly[(R)-3-hydroxybutyrate-co-4-hydroxybutyrate]/poly(ethylene glycol) graft TEMPO-oxidized cellulose nanofiber blends

*Pages 529-536*

Jiaqi Zhang, Shuji Fujizawa, Akira Isogai, Takaaki Hikima, Masaki Takata, Tadahisa Iwata

## Journal Metrics

- Source Normalized Impact per Paper (SNIP): **1.856**  
**Source Normalized Impact per Paper (SNIP):**  
2014: 1.856  
SNIP measures contextual citation impact by weighting citations based on the total number of citations in a subject field.
  - SCImago Journal Rank (SJR): **1.201**
- 

### **SCImago Journal Rank (SJR):**

2014: 1.201

SJR is a prestige metric based on the idea that not all citations are the same. SJR uses a similar algorithm as the Google page rank; it provides a quantitative and a qualitative measure of the journal's impact.

---

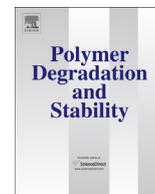
- Impact Factor: **3.163**  
**Impact Factor:**  
2014: 3.163  
The Impact Factor measures the average number of citations received in a particular year by papers published in the journal during the two preceding years.  
© Thomson Reuters Journal Citation Reports 2015
- 

- 5-Year Impact Factor: **3.722**  
**Five-Year Impact Factor:**

2014: 3.722

To calculate the five year Impact Factor, citations are counted in 2014 to the previous five years and divided by the source items published in the previous five years.

© Journal Citation Reports 2015, Published by Thomson Reuters



## Degradation of chitosan by sonication in very-low-concentration acetic acid



Emma Savitri\*, Sri Rachmania Juliastuti, Anitarakhmi Handaratri, Sumarno, Achmad Roesyadi

Institute Technology of Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

### ARTICLE INFO

#### Article history:

Received 23 April 2014

Received in revised form

10 September 2014

Accepted 16 September 2014

Available online 2 October 2014

#### Keywords:

Chitosan

Sonication

Acetic acid

Oligomers

Glucosamine

### ABSTRACT

Chitosan is a linear copolymer composed of (1 → 4)-linked 2-acetamido-2-deoxy-β-D-glucan (GlcNAc) and 2-amino-2-deoxy-β-D-glucan (GlcN) units in varying proportions, having a high molecular weight and strong intra- and intermolecular hydrogen bondings. Sonication has become an alternative for degrading chitosan into low-molecular-weight chitosan (LMWC), chitosan oligomers and glucosamine. In this study, chitosan was treated with sonication at 40 °C and 60 °C for 30 min and 120 min with various acetic acid concentrations (0.2% v/v–1% v/v); the very-low-concentration acid solution functioned both as a solvent and catalyst. After sonication, the samples were tested for changes in molecular weight, water soluble proportion of chitosan (chitosan oligomers and glucosamine), degree of deacetylation, degree of crystallinity, and morphology. The soluble and insoluble product yields at low concentration (0.5% v/v) at 40 and 60 °C were 33.66–39.37% and 32.43–34.26%, respectively. The main product was 5-hydroxy methyl furfural with composition 92.16–99.43%. At high concentrations (1% v/v), the soluble product and insoluble yields were 43.72–49.74% and 43.1–50.26%, respectively. The main product was glucosamine with composition 77.75–93.16% of glucosamine. There were changes in the morphology and crystallinity of the degraded chitosan, but no change in the chemical structure. The crystallinity had a tendency to increase. The degree of deacetylation tended to decrease due to the glucosamine breakage.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Chitosan is a linear copolymer consisting of (1 → 4)-linked 2-acetamido-2-deoxy-β-D-glucan (GlcNAc) and 2-amino-2-deoxy-β-D-glucan (GlcN) units in varying proportions. It is the most important derivative of chitin. A number of chitosan derivatives, such as low-molecular-weight chitosan (LMWC), chitosan oligomers (COS) and glucosamine have high potentials for use in medical and pharmaceutical applications, especially COS, that has uses as drugs for asthma [1–4], as antibacterial agents [5], as substances in wound-dressings [6,7], as vectors in gene-therapy [8,9], and as glucose level control in diabetics [10–14].

A number of chitosan degradation methods, such as chemical hydrolysis [15–17], oxidative-reductive degradation [18–21], and enzymatic treatments [22] were reported to produce low-molecular-weight chitosan (LMWC) and chitosan oligomers (COS). Chemical hydrolysis uses both strong and weak acids as hydrolysis agents to attain glucosamine and oligochitosan. Utilizing high

concentrations of acids has some environmental issues, but produces high yields of small fragments and high rates of chitosan hydrolysis. Furthermore, an excess acid treatment results in the degradation of glucosamine, which significantly reduces the yield [15–17]. The enzymatic process generally takes place under mild conditions, but the reaction rate is slow. Furthermore, the enzyme prices are high and the enzymes are not easily controlled [23,24]. Oxidative degradation in concentrated nitrous acid provides oligochitosan with 9–18 monomeric units, and the end products contained 2,5-anhydromannose residues by deamination [17].

The utilization of very low concentrations of weak acids combined with sonication might provide an alternative method to strong acid hydrolysis, even though the degradation reaction rate will be lower. Acetic acid is the weak acid used, and it also functions as a solvent. The concentration used was usually 6–12 wt% [25] whereas 1–2% v/v concentrations were also evaluated [26,27]. Below this limit, chitosan will either only partially dissolve or not dissolve at all. The acid provides the H<sup>+</sup> that will protonate the amine groups of chitosan. If the number of hydrogen ions is sufficient to balance the number of amine groups, it will be completely dissolved.

\* Corresponding author.

E-mail address: [savitri\\_ma@yahoo.com](mailto:savitri_ma@yahoo.com) (E. Savitri).