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

Emma Savitri*, Siti Rachmania Juliastuti, Anitarakhmi Handaratri, Sumarno, Achmad Roesyadi

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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.

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  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): **1.201i**

  SCImago Journal Rank (SJR):
  2014: 1.201
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  2014: 3.163
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- 5-Year Impact Factor: **3.722iFive-Year Impact Factor:**
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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

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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.

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, eventhough 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^+ 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 (E. Savitri).

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