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Thermal and microbial degradation of alginate-based superabsorbent polymer

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ABSTRACT

In this study, an alginate-based superabsorbent polymer (SAP), alginate-*graft*-poly[acrylamide-*co*-(itaconic acid)-*g*-(acrylic acid)] or Alg-*g*-P(AM-*co*-IA-*g*-AA), was prepared to examine its thermal and microbial degradation properties through Thermogravimetric Analysis (TGA), and soil supernatant test (with and without added nutrient) and soil burial test, respectively. The TGA thermogram of the SAP showed three degradation steps. The first degradation step was due to the thermal degradation of alginate and decomposition of the functional groups of PAM, PIA and PAA; whereas the second degradation step occurred as a result of the decomposition of PAM, PAA and PIA chains. Further decomposition of PIA contributed to the third degradation step. Among all the soil samples [tropical forest soil (TF), former tin mine lake soil (TM), peanut farm soil (PF), indigenous microorganism soil from an organic vegetable farm (OF), and oil palm plantation soil (OP)] tested, OF soil degraded the polymer sample most effectively, with the highest weight loss of 82.6% (with added nutrient) and 82.8% (without added nutrient) in soil supernatant tests, and 63.5% in soil burial test. Morphological observation under an Illuminated Stereo Microscope showed some holes and weak topographical spots on the surface of the polymer material after it had been incubated in OF solution for 40 days. Meanwhile, the intrinsic viscosities, [η], of NaAlg and the Alg-based SAP solutions were 2.62 and 2.75 respectively.

1. Introduction

Alginic acid is a naturally occurring acidic polysaccharide majorly extracted from the brown algae (phylum Phaeophyta). It exists as the most abundant polysaccharide in the brown algae, consisting of up to 40% of the dry matter [1]. Alginic acid is an unbranched block copolymer consisting of two distinct monosaccharide residues, (1,4)-β-D-mannuronic acid (M) and (1,4)-α-L-guluronic acid (G).

Alginates do not have any nutritional value; nevertheless, they are frequently used as additives to alter and stabilize the texture of foods. Other than being used as traditional wound dressings, alginates are also used in dental impression material and in some formulations preventing gastric reflux [2]. Apart from these, alginate has gained immense popularity in textile printing as a shear-thinning viscosifyer due to its resulting color yield, brightness and print levelness.

Holme et al. [3] commented that the depolymerization of polysaccharides occurs via cleavage of the glycosidic bonds. The glycosidic linkages of alginates are believed to be susceptible to a variety of degradation mechanisms, including oxidative–reductive free radical depolymerization (ORD-reaction), acid-, alkaline- and enzymatic-catalyzed hydrolysis.

Smidsrød et al. [4], as cited by Holme et al. [3], were mentioned to have proven that the presence of oxygen affects the stability of non-purified alginates due to the presence of phenolic reducing substances which give rise to the ORD-reaction. Meanwhile Oates and Ledward [5] reported that alginate undergoes extensive decomposition when it is exposed to temperatures above 250 °C.

Changes brought about by degradation are not necessarily at all undesirable, in biodegradation or cases where deliberate lowering of the molecular mass of a polymer is called for, these changes turned desirable. In recent years, interest in polymer production has shifted towards the synthesis of biodegradable polymers due to their environmental benefits.

Biodegradable polymers are a type of macromolecules which are able to break down into smaller compounds or completely degrade in biologically active environments [6]. Although the breakdown process is normally known to be caused by microorganisms [7], biodegradation can also occur through hydrolysis and oxidation processes in biological environment.

Biodegradable polymer can be applied into many aspects of life, for example, in environment friendly packaging materials, agriculture, drug delivery, gene delivery, etc. One of the most successful applications for biodegradable polymers is in biomedical field [8]. There is a wide variety of natural and synthetic biodegradable polymers that

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have been used for these applications [9]. Examples of natural biodegradable polymers that have been used are collagen, albumin, gelatin and chitin. However due to their high cost and questionable purity, synthetic biodegradable polymers (polylactide or polymers from microbial fermentation such as polyhydroxybutyrate) which are reported to be free from most of the problems associated with natural polymers have been increasingly used [9].

Considering the importance of alginates and the lack of information about the thermal and microbial behavior of SAP incorporated with alginates, the present work describes the thermal and biodegradation of the Alg-based SAP (Fig. 1) [10], in which the SAP was synthesized by grafting of acrylamide, itaconic acid and acrylic acid onto alginate backbone.

Viscosity measurement offers the simplest and most extensively used technique for determining molecular masses. In this study, the molecular masses of NaAlg and the Alg-based SAP were investigated using the viscosity method. The thermal degradability of the SAP was investigated by thermogravimetry (TG) while the biodegradability was examined in five different types of soil samples, namely tropical forest soil (TF), former tin mine lake soil (TM), peanut farm soil (PF), indigenous microorganism soil from an organic vegetable farm (OF), and oil palm plantation soil (OP). In order to compare the effects of the biodegradability among the five soil samples, soil supernatant test (with and without added nutrient) and soil burial test were carried out. In addition, the structure and morphological changes of polymer samples incubated in soil solutions were observed under an Illuminated Stereo Microscope.

2. Materials and methods

2.1. Chemical reagents

The graft copolymerization process was carried out by using sodium alginate (NaAlg, R&M, UK) as the backbone polymer and acrylamide (AM, R&M, UK), itaconic acid (IA, Fluka, China), and acrylic acid (AA, R&M, UK) as the monomers. Sodium bicarbonate (SBC, Dulab, Malaysia) was used as neutralizing agent. Calcium chloride dihydrate (Systerm, Malaysia) was used to gel the SAP. In the viscometry test, sodium chloride (NaCl, J. Kollin, UK) was used to prepare 0.1 M NaCl solution.

The chemicals used in biodegradation analysis were zinc sulfate and sodium chloride (Systerm, Malaysia), iron (II) sulfate and magnesium sulfate (Fisher Scientific, UK), manganese (II) sulfate monohydrate (Ajax Finechem, Australia) and multivitamins (Sunward Pharmaceutical, Malaysia).

2.2. Synthesis of Alg-based SAP

A certain amount of NaAlg was dispersed with distilled water in a beaker. The system was heated at 80 ± 2 °C with stirring for 30 min to form a homogenous, gelatinized paste.

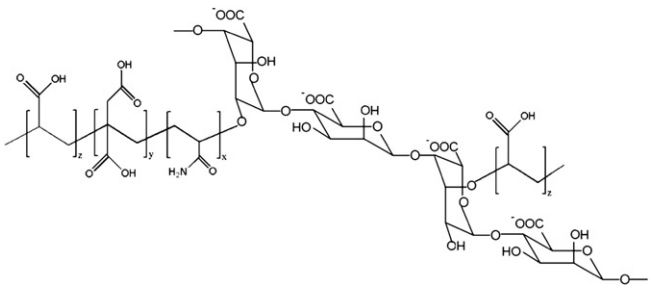

Fig. 1. Chemical structure of Alg-based SAP.

After cooling the gelatinized NaAlg to 45 °C, a mixture of distilled water, AM (if any), and IA was added into it, followed by the initiator to initiate the reaction. SBC was added to neutralize the reaction mixture. The system was stirred sufficiently for 30 min.

AA (if any, AM:IA:AA = 8:1:1) was later added into the reaction mixture, followed by the initiator. SBC was again added almost immediately after that. The system was stirred for another 30 min until completion.

2.3. Viscometry measurement

2.3.1. Preparation of NaAlg and Alg-based SAP solution

The NaAlg gel that was prepared via the method described in Section 2.2 (not including AM, IA and AA) was weighed accurately and dissolved in roughly 20 mL of 0.1 M NaCl. The solution was then transferred into a 25 mL volumetric flask and it was topped up to 25 mL with 0.1 M NaCl to give a 0.1% w/v NaAlg solution.

The 0.1% w/v Alg-based SAP solution was prepared likewise as the NaAlg solution.

2.3.2. Determination of solvent flow time, t_o

A water bath was set to 30 °C. Ten mL of 0.1 M NaCl was pipetted into an Ubbelohde viscometer (size OB) which was suspended in the water bath.

The system was allowed to attain thermal equilibrium for at least 10 min before the solvent flow time, t_o, was measured using a stop-watch. The average of the three most consistent readings was taken as t_o.

2.3.3. Determination of solution flow time, t

Ten mL of 0.1% w/v NaAlg (or Alg-based SAP solution) was pipetted into the viscometer. The system was allowed to attain thermal equilibrium for at least 10 min, before the solution flow time, t, was measured. The average of three readings was taken as the t.

The concentration of the solution in the viscometer was reduced by adding 1 mL of 0.1 M NaCl into the viscometer. To ensure homogeneous mixing, the viscometer was well-shaken for a minute. The system was then allowed to attain thermal equilibrium for at least 3 min before the solution flow time was determined. The dilution was repeated five to six times, each time by adding 1 mL of 0.1 M NaCl into the viscometer. For each concentration, the measurement of flow time was done thrice and the average value was calculated.

The value of t_0 is subtracted from t; the thus obtained result is divided by t_0 to attain the specific viscosity, η_{sp}. When η_{sp} is divided by the concentration c of the polymer, the Huggins equation is obtained as follows:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

where k' is a dimensionless parameter (the Huggins coefficient) which value depends upon temperature as well as the specific polymer/solvent combination.

The ratio η_{sp}/c is commonly called the reduced viscosity, η_{red}. When η_{red} is plotted against the concentration c of the polymer, the y-intercept of the plot gives the intrinsic viscosity, $[\eta]$.

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (Mettler Toledo TGA SDTA851e) was carried out using sample masses between 1 and 5 mg weighed in a standard 150 μL alumina sample holder. The sample was analyzed in nitrogen atmosphere at a flow rate of 20 mL/min. The temperature range investigated was from ambient temperature to 900 °C at a heating rate of 20 °C/min.