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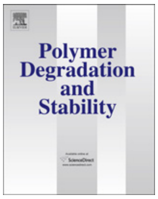

The synthesis conditions, characterizations and thermal degradation studies of an etherified starch from an unconventional source

O.S. Lawal [a,b,*], M.D. Lechner [c], W.M. Kulicke [b]

[a] Department of Chemical Sciences, Olabisi Onabanjo University, P.M.B 2002, Ago-Iwoye, Ogun State, Nigeria
[b] Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundestrasse 45, D-20146 Hamburg, Germany
[c] Institute of Physical Chemistry, University of Osnabrück, Babarastrasse 7, 49069 Osnabrück, Germany

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ABSTRACT

Starch isolated from an under-utilized legume plant (pigeon pea) was carboxymethylated. Influences of reaction parameters were investigated on the degree of substitution (DS) and the reaction efficiency (RE). Studies showed that optimal DS of 1.12 could be reached at reaction efficiency of 80.6% in isopropanol–water reaction medium (40 °C, 3 h). Scanning electron microscopy showed that after carboxymethylation, the granular appearance of the native starch was distorted. Wide-angle X-ray diffractometry revealed that crystallinity was reduced significantly after carboxymethylation. The infrared spectra revealed new bands in the carboxymethyl starch at $\nu = 1600, 1426$ and $1324\ \text{cm}^{-1}$ which were attributed to carbonyl functional groups vibration, –CH_2 scissoring and OH bending vibration, respectively. Broad-band ^{13}C NMR of carboxymethyl starch showed an intense peak at $\delta = 180.3$ ppm which was assigned to carbonyl carbon on the carboxymethyl substituent on the AGU (Anhydroglucose Unit). DEPT (Distortionless Enhancement by Polarization Transfer) 135 NMR showed negative signals which correspond to methylene carbons on the AGU. Differential Scanning Calorimetry (DSC) suggests loss of crystallinity after carboxymethylation. Thermogravimetry (TG), Derivative Thermogravimetry (DTG) and Differential Thermal Analysis (DTA) show that thermal stability improved after carboxymethylation. The study provides information on the preparation and characterization of a biomaterial from a new source which could be used alone or in the preparation of other functional polymers for diverse polymer applications.

1. Introduction

Starch derivatives play vital roles in the burgeoning biopolymers industries. This is because they are cheap, non-toxic, renewable and compatible with many other materials for industrial applications. Diverse polymer applications use starch derivatives directly or after they have been combined with other synthetic polymers. Applications in food [1,2], environmental management [3–5], agriculture [6], pharmacy [7], biomedical engineering [8] and textiles [9] have been reported widely in the literature.

Unfortunately, using starch in its native form is often limited by certain undesirable characteristics such as poor solubility, low mechanical properties and instability at high temperature, pH and shear during processing. Hence it is always reasonable to modify it to suit specific industrial process. Chemical modification of starch involves reaction of the hydroxyl groups on the AGU and these have been used to produce starch derivatives based on oxidation [10], acetylation [11], hydroxypropylation [12], carboxymethylation [13] and cross-linking [14].

Among starch derivatives, etherified starches such as carboxymethyl starch (CMS) have attracted a lot of attention in recent years. Carboxymethyl starches are usually synthesized by the reaction of starch with monochloroacetic acid or its sodium salt after activation of the polymer with aqueous NaOH in a slurry in an aqueous organic solvent, in most cases an alcohol. Different approaches have also been reported in the literature for the synthesis of carboxymethyl starch. This include induced phase separation method using dimethyl sulphoxide [15], synthesis of 2,3-di-*O*-carboxymethyl starch via 6-*O*-triphenylmethyl [16], carboxymethylation after γ irradiation [17], carboxymethylation after starch oxidation [18] and using of various organic solvents such as ethanol, methanol, isopropanol, butanol, and acetone [19]. The aim of all these approaches is to synthesize carboxymethyl starch at optimized conditions such as high product yield, high reaction efficiency as well as high DS. The DS is an indication of the amount of carboxymethyl group formed on the starch molecule. Technically, the DS is defined as the average number of substituent per AGU. The functional properties of CMS are dependent on the DS. Such properties include the viscosity of the solution, film forming

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[*] Corresponding author. Department of Chemical Sciences, Olabisi Onabanjo University, P.M.B 2002, Ago-Iwoye, Ogun State, Nigeria. Tel.: +234 7033268164.
E-mail address: laidelawal2@yahoo.com (O.S. Lawal).

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properties, interaction with cations, formation of supramolecular aggregates and rheological properties. In our previous publications, we reported on the synthesis of CMS using cocoyam starch [20]. Also, in a recent work, we reported the synthesis of CMS using water yam starch [13]. In the literature, starches from other origins have also been used for the synthesis of carboxymethyl starch and these include potato starch [21], rice starch [22], corn starch, amaranth starch [19], cassava starch [23] and mung bean starch [24]. However, the increasing demand for starch and derivatised starches in the ever-increasing biopolymer based industries justifies the need for the exploration of new resources for starch, particularly, cheaper alternatives to conventional sources such as potato and maize.

In the present investigation, pigeon pea was used as the source of starch for carboxymethylation. Pigeon pea is a woody perennial legume crop belonging to the family Fabaceae. It is cultivated throughout the world in both tropical and sub-tropical regions. In Nigeria and India, it is used both as a food and as a cover crop. Studies have revealed that pigeon pea contains between 57.3% carbohydrate, 19.2% protein, 1.5% fat and 8.1% fiber [25]. The rich carbohydrate content of pigeon pea suggests that it is a reasonable source of starch.

The authors are cognizant of the fact that CMS is a vital raw material for the synthesis of other functional bio-based polymers. Hence, the concern of the present investigation is to explore the preparation of a valuable biomaterial from a relatively cheap and under-utilized source of starch (pigeon pea). The authors are not aware of any previous publication concerning preparation and the polymer characterization of carboxymethyl starch from pigeon pea. Hence, preparation, characterization and polymer stability studies of CMS based on pigeon pea are presented herein.

2. Materials and methods

2.1. Materials

Pigeon pea was donated by the International Institute of Tropical Agriculture, Ibadan, Nigeria. Sodium hydroxide and sodium monochloroacetate were purchased from Merck Schuchardt, Germany. Isopropanol, methanol, ethanol, *tert*-butanol, and acetone were of technical grade. All other reagents were of analytical grade.

2.2. Isolation and purification of pigeon pea starch

Starch isolation was carried out using the method described by Adebowale and Lawal [26]. The yield of the starch obtained was 22.5% and the result of the analyses of the composition using AOAC methods [27] was moisture, 8.2%; ash, 0.7%; fat, 0.5%; crude fiber, 0.8%; protein, 2.5%; carbohydrate, 87.3%; pH, 7.9. It was washed twice before drying in the air for 48 h at 30 ± 2 °C. The native pigeon pea starch obtained (NPPS) was stored in polythene bag at 30 ± 2 °C until use.

2.3. Preparation of carboxymethyl starch

For the preparation of carboxymethyl pigeon pea starch (CMP), NaOH of different quantities (8–16 g) was added to water in a 2 L three-necked round-bottomed flask equipped with motor driven stirrer and the mixture was stirred at 250 rpm until complete dissolution of sodium hydroxide was observed. Organic solvent (500 mL) was added to the solution in each case and the temperature was raised to between 30 and 60 °C. Organic solvents used in this experiment were isopropanol, methanol, ethanol, and *tert*-butanol. The water content in the reaction mixture was varied between 40 and 80 mL (the moisture content of NPPS was predetermined). Starch (40 g dry wt) was added to the mixture and it was stirred at 400 rpm while nitrogen gas was flushed through the reaction mixture to maximize the reaction of NaOH with starch. After stirring for 1 h, SMCA (20–50 g) was added to the mixture and the reaction time was varied between 1 and 4 h following which the mixture was filtered, suspended in methanol and neutralized with acetic acid. Following filtration, the slurry was dispersed again in 80% methanol and it was washed several times until the filtrate gave negative response to silver nitrate test of the chloride. The slurry obtained was suspended in acetone, stirred for 20 min, and dried in an oven at 40 °C for 48 h.

2.4. Determination of degree of substitution

Titrimetry was used for the determination of the DS. CMS (10 g) was dispersed in acetone (300 mL) and 5 M HCl (30 mL) was added to the dispersion which was stirred for 30 min. During this process, the CMS which was in sodium form was converted to the H-CMS (carboxymethyl starch in hydrogen form). H-CMS was washed four times with 80% (v/v) methanol until the solution became neutral with pH test. The neutral dispersion was filtered again, suspended in acetone and it was stirred for another 15 min, following which it was filtered and dried for 24 h in a desiccator over silica gel. Two grams of H-CMS was dissolved in 1% (w/v) NaCl solution and it was titrated with 1 M NaOH. The DS was determined as follows.

$$\mathrm{DS} = \frac{n_{\mathrm{NaoH}} \times M_{\mathrm{o}}}{m_{\mathrm{c}} - n_{\mathrm{NaoH}} \times M_{\mathrm{R}}} \tag{1}$$

$$m_{\mathrm{c}} = m_{\mathrm{p}} - \left[\frac{m_{\mathrm{p}} \times F}{100}\right] \tag{2}$$

where M_o = molar mass of the anhydroglucose unit = 162 g/mol; M_R = molar mass of carboxymethyl residue = 58 g/mol; n_{NaOH} = quantity of sodium hydroxide used (mol); m_p = weight of polymer taken (g); m_c = corrected weight of polymer (g); F = moisture (%).

The DS_t is the theoretical degree of substitution. It is the maximal degree of substitution when the limiting reactant either SMCA or NaOH is totally used.

$$\mathrm{DS_t} = \frac{n_{\mathrm{SMCA,0}}}{n_{\mathrm{AGU,0}}} \text{ if } n_{\mathrm{NaoH,0}} \geq n_{\mathrm{SMCA,0}} \tag{3}$$

$$\mathrm{DS_t} = \frac{n_{\mathrm{NaoH,0}}}{n_{\mathrm{AGU,0}}} \text{ if } n_{\mathrm{NaoH,0}} < n_{\mathrm{SMCA,0}} \tag{4}$$

where n_{SMCA} = number of moles of sodium monochloroacetate; n_{AGU} = number of moles of anhydroglucose unit; n_{NaOH} = number of moles of sodium hydroxide.

The RE is a measure of the amount of carboxymethyl group bonded to the starch. The RE is defined as:

$$\mathrm{RE} = \frac{\mathrm{DS}{*}100}{\mathrm{DS_t}} \tag{5}$$

where the molar mass of the unsubstituted anhydroglucose unit = 162 g/mol and the molar mass of a substituted anhydroglucose unit = 242 g/mol.

2.5. Starch granule morphology

Starch granule morphology was examined with a Leo 1550 ultra scanning electron microscope. The samples were mounted on studs, sputter coated with gold (Balzers, SCD-040; Norderstedt, Germany) and examined under the scanning electron microscope.