ChemSearch Journal 7(1): 17 – 24, June, 2016
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 29/04/2016 Accepted: 04/05/2016
http://dx.doi.org/10.4314/csj.v7i1.3

Synthesis, Characterization and Sorption Potentials of Dialdehyde Starch Aminophenol Schiff's Base

[*]Salisu, A. A., Umar, A. S. and Kaila, H.
Department of Pure and Industrial Chemistry, Bayero Unuversity Kano, Nigeria
Email: aasalisu@yahoo.com

ABSTRACT

Extraction of native cassava starch, its oxidation, modification and chelation of the products were achieved. Schiff's base type Dialdehyde aminophenol was prepared by the reaction of orthoaminophenol and dialdehyde starch from periodate oxidized cassava starch. The modified starch aminophenols with different aldehyde content were tested for their adsorptive affinity for Cu(II), Cr(II) and Mn(II) ions. The modified starch was characterized by Fourier transformed infrared (FT-IR) spectroscopy, Scanning electron microscopy (SEM), elemental analysis, solubility test, Magnetic susceptibility and magnetic moment and, melting/decomposition temperature. The modified starches and the polymeric complexes have been found to have an improved physicochemical properties and the polymeric chelating ligand could be used to remove Cu(II), Cr(II)and Mn(II)ions from aqueous solution. Also the polymeric complex was found to have good cross linking ability when reacted with the metal salt.

Keywords: Dialdehyde starch, Native Starch, Orthoaminophenol, Polymeric Chelating ligand, Sorption

INTRODUCTION

Modified starch derivatives find a lot of applications in pharmaceuticals as disintegrant, binder in coated paper, in plastic industry and in medicine (Salisu *et al*., 2013). Among all methods of modification of native starch, oxidation is one method which produces a modified starch with interesting opportunities. Dialdehyde starch (DAS) from the periodate oxidative cleavage of the C_2-C_3 bond of the hydroglucose units of starch polysaccharide chains find several industrial applications (Fiedorowicz and Para, 2005). The oxidation reaction of starch is highly specific (Spence, *et al*, 1995), with the oxidizing agent cleaving the C_2-C_3 bond thus generating an aldehyde group on each of the two carbon atoms. There are generally four methods used to modify native starch viz: physical, chemical, enzymatic and biological methods (Akpa and Dagde, 2012, Liming, *et al*, 2011). Once the hydroxyl group of starch has been replaced with the aldehyde group, the starch shows greater hydrophobicity and the recrystallization of starch is inhibited. Cross linking has been reported to increase the shear stability, viscosity and pasting temperature of starch. The greater strength of the cross linked granule limits the breakdown of viscosity under shear, giving a resistance to breakdown (Liu, *et al*, 1999). Dual modification, i.e. a combination of substitution and cross linking has been demonstrated to provide stability against acid, thermal and mechanical degradation of starch and to delay retrogression during storage (Jaspreet, *et al*, 2007). Thus, crosslinking has been developed in order to harness the added potentials of this process.

When starch was subjected to the processes of modification, many of its Physico-chemical properties such as swelling, solubility thermal stability and light transmittance have been reported significantly to increased (Jaspreet, *et al*, 2007). An increase in gelatinization temperature has been observed for cross linked starches, which are related to the reduced mobility of amorphous chain bridges, as ΣH_{gel} of starch increases with increasing levels of cross linking (Liu *et al*., 2003). Dual modification, a combination of oxidation and crosslinking, has been demonstrated to provide stability against acid, thermal and mechanical degradation of starch and to delay retrogression during storage (Jaspreet *et al*., 2007).

Heavy metal pollution is one area of particular interest where the application of modified starch as polymeric resin is of utmost importance. The danger of toxic effect and accumulation of heavy metals throughout the food chain and ultimately the human body calls for special concern. By using adsorption method of trapping these heavy metals from aqueous solutions on to the dialdehyde starch polymer matrices, especially when it contains metal-chelating ligands containing one or more electron donor atoms like nitrogen, oxygen, sulphur and phosphorous, which can form coordinating bonds with heavy metals (Feng-Yin, *et al*., 2007), there is the possibility of controlling the effect of these heavy metal pollution. This is possible because Schiff `s base (C=N) can easily form complexes with transition metal ions.

Many polymer matrixes containing Schiff base or thiazole ligands were investigated to adsorb Cu (II) ions (Qiang *et al*., 2008).Starch aldehyde 2-amino-4,6-dihydroxylpyrimidine (DASAP) was synthesized by the reaction of 2-amino-4,6-dihydroxylpyrimidine and dialdehyde starch (DIAS) from periodate oxidized corn starch, and was employed to adsorb Cu (II) ions from aqueous media (Awokoya *et al.*, 2013). Starch-urea-based biodegradable coordination polymer modified by transition metals Mn(II), Co(II), Ni(II) Cu(II), and Zn(II) were prepared by polycondensation of starch and urea. The thermogravimetric analysis of the complexes revealed that all the polymeric metal complexes are more thermally stable than the parental ligand (Ashraf *et al.*, 2010).

In this paper, orthoaminophenol has been used to modify dialdehyde starch, through Schiff base formation and at the same time provide reaction site for the formation of the coordinating bond between the modified starch polymer and the heavy metals.

MATERIALS AND METHODS

Materials

Freshly harvested Cassava tubers were purchased from Garu village in Madobi Local Government Area of Kano State, Nigeria. All chemicals were used as procured without further purification. Sodium periodate was purchased from (Sigma Aldrich). Copper (II) chloride, Manganese (II) chloride and chromium (II) chloride, orthoaminophenol, sodium hydroxide, sodium acetate buffer, sulphuric acid and acetic acid were purchased from (Across). Infrared spectra were obtained using the KBr disc technique with FTIR 8400s – SHIMADZU. The photomicrographs were obtained from Scanning Electron microscopy (SEM) (Phenom ProX and energy dispersive x-ray spectroscopy (EDX) optical magnification 80-130,000x). Magnetic Suscesstabilty Machine (Agilent technologies).

Extraction of Starch and Preparation of Dialdehyde Starch

Freshly harvested Cassava starch was extracted according to the procedure reported by Akpa and Dagde, (2012). The tubers were peeled, washed and disintegrated in a grating machine, after which the resulting mesh was reground and mixed with water in the ratio 1:5 (W/V). The mesh was filtered using a double layer of nylon cloth filter to obtain the starch solution. The resulting solution was allowed to settle and later the water was decanted and the residue set in an oven to dry. The dried native cassava starch was converted to Dialdehyde starch following the procedure reported by Feng-Yin, *et al.* (2007). The dried cassava starch (20.0g) was suspended in 80ml of distilled water and mixed with various amounts of sodium periodate (13.2g, 19.8 and 26.4g). The suspension was adjusted to pH 3 by the addition of sodium acetate buffer and incubated in a water bath at 35^0C for 4hrs. The product was then washed with 250ml distilled water and 50ml acetone. The dialdehyde starch formed was then dried in an oven at 50^0C to constant weight and stored at 25^0C.

Determination of Aldehyde Content

The dialdehyde starch was subjected to aldehyde content determination using rapid quantitative alkali consumption method (Feng – Yin *et al.*, 2007). The dried Dialdehyde starch (DAS) (0.2g) was weighed into a flask and swirled in a water bath set at 70^0C for 2 minutes and then cooled immediately under running tap water for a minute. 10ml of standardized 0.2M H_2SO_4, 50ml of water and 1ml neutral 0.2% phenolphthalein were added, and the solution was titrated using 0.2M NaOH (Jasmein *et al.*, 2014).

Preparation of Dialdehyde Starch Aminophenol (DASAPh)

Modification of the dialdehyde starch was achieved by mixing 12.9g dry DAS with 100ml distilled water in a 500ml three-necked flask, equipped with a mechanical stirrer and thermostat water bath, maintained at 50^0C for 4hrs. A solution of 2-aminophenol (0.2M) was slowly introduced drop wise into the flask under nitrogen, and pH of the reaction was adjusted to 5.0 by adding sodium acetate. The solution was filtered and then washed three times with distilled water (3 x 100ml) and oven-dried at 50^0C to constant weight (Grommers *et al.*, 2009).

Sorption Experiment

The adsorption experiment for heavy metal ions was carried out using batch adsorption method as outlined by Feng–Yin *et al*. (2007). Series of 100ml flasks, containing the desired dose of (0.5g) dialdehyde starch aminophenol, and 50ml of the heavy metal salt solutions at the desired concentration (0.1M) were shaken on a shaking bath. The initial pH of the solution was adjusted with acetic acid to 5.0 before adding the adsorbent. After shaking for 90 min to ensure full equilibration, the mixture was centrifuged at 4000 r/m for 20 min and filtered.

Melting Temperature

Determination of melting temperature was achieved using melting temperature apparatus. 20mg of the dialdehyde starch aminophenol was placed in the capillary tube and inserted into the apparatus and the melting temperature reading was determined in ^{0}C (Grace 1977).

FT-IR Spectral Analysis

Infra red spectra of the compounds were obtained using a Shimadzu FTIR 8400s in the region 4000-400cm^{-1} using KBr disc pellet technique. The bands of interest were selected and interpreted accordingly.

Solubility Test

The solubility of the compounds was determined in various solvents. These solvents were water, dimethylsulfoxide, Dimethylformamide, ethanol, ether and acetone and the results were tabulated.

Magnetic Susceptibility and Magnetic Moment

Magnetic susceptibility tests were carried out using magnetic susceptibility machine. The sample was grounded using pestle and mortar, after which it was introduced into the tube and allowed to come to temperature equilibrium before taking the measurement. Magnetic moment was calculated from the results of magnetic susceptibility (Awokoya *et al.*, 2013).

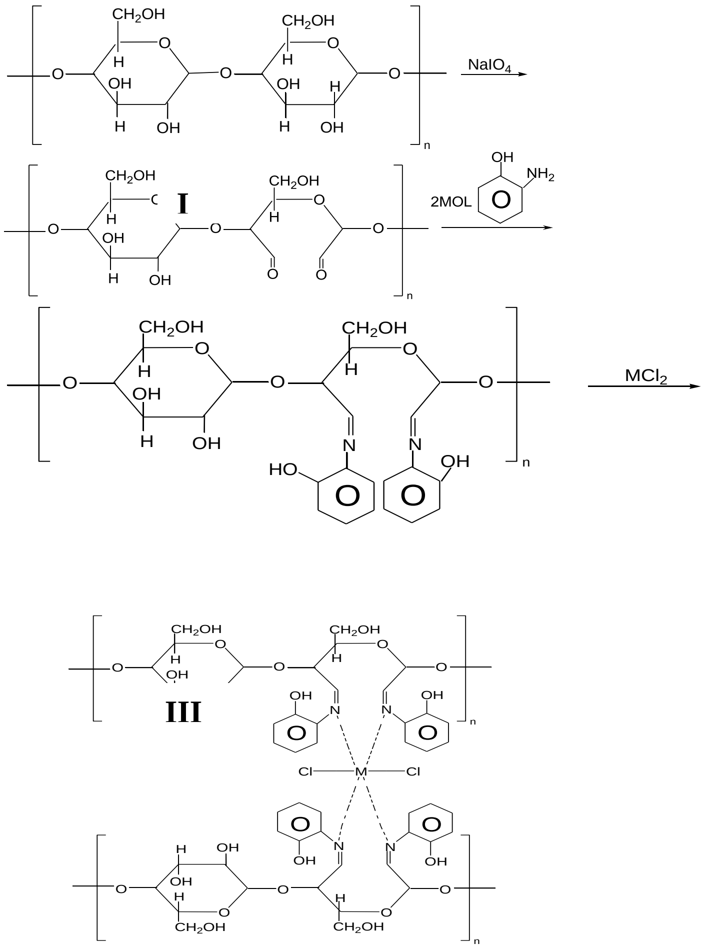
Scanning Electron Microscopy

Studies on granule morphology of the compounds were conducted using Scanning Electron Microscope in order to determine the extents of the modifications.

RESULTS AND DISCUSSION

Synthesis

The reaction process of dialdehyde starch aminophenol proceeded as presented in scheme **1**. The starch polymer **I** was subjected to sodium periodates ($NaIO_4$) oxidation. The sodium periodate, being a selective oxidant that cleaved the C_2-C_3 of the anhydroglucose units in the native starch to form the dialdehyde groups in compound **II**; the dialdehyde starch polymer was reacted with 2 moles equivalent of orthoaminophenol to produce the modified starch aminophenol Schiff's base compound **III**.



Scheme 1: Route to the dialdehyde starch, dialdehyde starch aminophenol and the cross linked modified starch metal chelates (Present study)

The ligands were further reacted with some transition metal chlorides, namely Cu(II), Cr(II) and Mn(II) chlorides, which resulted in the production of the cross-linked modified starch polymer metal chelates **IV**

Preparation of dialdehyde Starch

Three different dialdehyde starches were prepared and were designated DAS-1, DAS-2 and DAS-3. The solution of the dialdehyde starch was titrated using 0.2M NaOH and the percentage of the dialdehyde unit was determined using equation (1):

$$\text{Da\%} = \frac{[(V_1C_1 - 2(V_2C_2)]}{W/161} \times 100 \qquad (1)$$

Where, V_1, V_2 and W represent the total volume of H_2SO_4, volume of NaOH and dry weight (g) of the DAS respectively. C_1, C_2 (M) are the concentrations of H_2SO_4 and NaOH respectively. 161 is the average molecular weight of the repeat unit in dialdehyde starch (Liu *et al.*, 2003).

The percentage of dialdehyde units in the DAS's were fund to be 70.16%, 87.09% and 94.35% respectively, using rapid quantitative alkali consumption method and results are presented in Table 1

Table 1: Aldehyde Content of the Dialdehyde Starch

Product	Average titre values (cm^3)	Aldehyde content (%)
DAS-1	24.33	70.16
DAS-2	25.41	87.09
DAS-3	25.87	94.35

Modification of the Dialdehyde Starch

The dialdehyde starch (DAS's) was reacted with stoichiometric amounts of 2–aminophenol in the ratio of 1:2 to form the modified Dialdehyde starch aminophenol derivatives. The colour of the dialdehyde starches and the degree of substitution are given in Table 2. The degree of substitution of 2-aminophenol, which represents the average molecular number of the repeat unit in the DASAPh, was theoretically calculated and found to be 0.44, from the nitrogen content using equation (2) (Awokoya *et al.,* 2013) and results are presented in Table **2**

$$\textbf{DS} = \frac{161 \times N\%}{(28 - 109.13 \times N\%)} \qquad (2)$$

Where DS is the degree of substitution, 161 is the average molecular weight of repeat unit and N% is the nitrogen percentage in the modified starch. The highly selective nature of the oxidizing agent ($NaIO_4$) in the formation of the dialdehyde groups on C_2 and C_3 formed the basis of this work.

Table 2: Degree of substitution, Colour, Yield and Elemental Analysis for DASAPhs

Product	Reactant	Colour	Yield (%)	Elemental Composition			DS
				N%	C%	H%	
DASAPh-1	DAS-1	Dark brown	70.16	5.90	42.9	6.17	0.44
DASAPh-2	DAS-2	Light brown	87.09	12.34	43.56	5.23	0.43
DASAPh-3	DAS-3	Brown	94.35	13.56	46.18	6.98	0.45

The reaction showed a very remarkable increase in aldehyde content with increasing amount of the periodate (70.16%, 87.09% and 94.35% for 13.2g, 19.8g and 26.4g of periodate respectively) as shown in Table 2. These could be due to the increase in concentration of the oxidant which leads to the high breaking down of the C_2 and C_3 bond in the anhydrous glucose unit of the starch to yield the dialdehyde modified starch. This aldehyde group provided the reaction site for the 2–aminophenol to react with the starch. The percentage yields for DASAPh 1, 2 and 3 were calculated using equation (3) (Liu *et al.,* 2003).

$$\%\,\boldsymbol{Yield} = \frac{\boldsymbol{experimental\ weight}}{\boldsymbol{theoritical\ weight}}\ \boldsymbol{X\ 100} \qquad (3)$$

Where, experimental weight = experimental mass of the samples, theoretical weight = calculated mass of the samples.

The products were in good yield and gave dark brown, light brown and brown colours for DASAPh-1, DASAPh-2 and DASAPh-3 respectively. Moreover, it can be seen that the nitrogen content, the percentage yield and degree of substitution in DASAPhs increased from DASAPh-1 to DASAPh-3, these could be due to the increase in the amount of the oxidizing agent (i,e sodium periodate) concentration (Liu *et al.*, 2003).

Melting/Decomposition Temperature

The successive increase in the Melting temperatures of these compounds indicated the successful synthesis of the modified starch and the complexes.

Table 3: Melting Temperatures of the Modified polymers

Product	Melting Temp. (^{0}C)
DAS	211
DASAPh	219
DASAPh-Cu	301
DASAPh-Cr	305
DASAPh-Mn	316

The DAS melted at 211^{0}C, the modified starch at 219^{0}C while the modified starch polymer-metal complexes melted with decomposed at 301^{0}C, 305^{0}C and 316^{0}C respectively. These can be attributed to the progressive increase in the molecular masses of the compounds as indicated in Table 3.

FT –IR Analysis*:*

The infrared spectra of the compounds under investigations were recorded in the region of 4000 – 400cm^{-1} with Shimadzu – FTIR – 8400s, using KBr disc pellet technique. It can be seen that the characteristic broad band for OH stretching at 3395cm^{-1} (Figure 1), began to diminish with formation of the aldehyde groups and the carbonyl groups bands observed at 1724cm^{-1}. This shows that the DAS has been successfully produced, and the increase in the intensity of the band showed an increase in the aldehyde content in DAS1, DAS2 and DAS3 respectively.

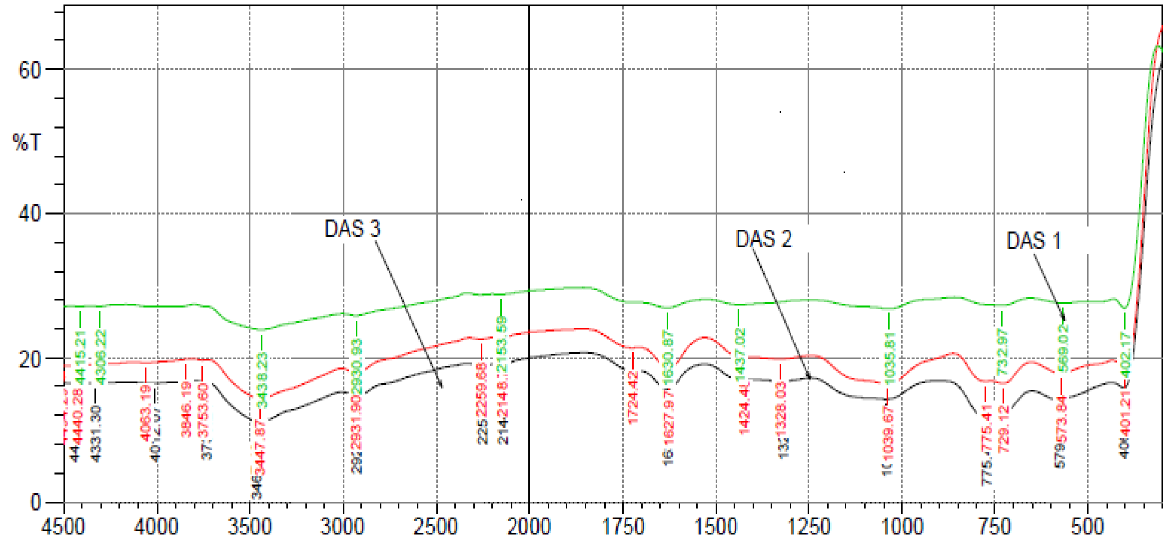


Figure 1: FT-IR Spectra for the DAS1, DAS2 and DAS3

The presence of bands at 1195cm^{-1}, 1199cm^{-1}, and 1275cm^{-1}can be assigned to the substituted phenol (2-aminophenol) used as the reagent for modification of the DAS and amino substitution was confirmed at 1582cm^{-1} thus, confirming the success of the modification. The band at 1628cm^{-1} for C=N indicated that Schiff`s base between DAS and aminophenol was formed.

Solubility Test

The modified and cross-linked polymers were found to be soluble in some solvents like Dimethylformamide, acetone and DMSO but slightly soluble in water, ethanol and ether as showed in Table 5**.**

Table 5: Solubility of Dialdehyde starch aminophenol

Solvent	Solubility
Water	**SS**
DMSO	**S**
DMF	**S**
Ethanol	**SS**
Ether	**SS**
Acetone	**S**

S=Soluble, SS= slightly soluble

Magnetic Susceptibility and Magnetic Moment

The Magnetic susceptibility, which is a dimensionless proportionality, is a quantitative measure of the extent to which a material may be magnetized in relation to a given applied magnetic field. This value equals the ratio of the magnetization within the material to the applied magnetic strength. The values were calculated using equation (4) and presented in Table 6;

$$\boldsymbol{Xg = \frac{C\ X\ L\ (R - R_0)}{10^9\ M}} \quad (4)$$

Where: C = 1, a constant, L = sample length in the tube in cm, R = Reading obtained of sample + tube, R_0 reading obtained of pre-weighed empty tube, M = Mass of the sample in the tube in gram. The values obtained for Magnetic Susceptibility and Magnetic Moment are presented in Table 6 (Liu *et al.,* 2003)

Table 6: Magnetic Susceptibility and Magnetic Moment Values

Product	Mag susceptibility(¯g)	Mag Moment(BM)
DASAPh-Cu	$8.9x10^{-6}$	0.202×10^{-1}
DASAPh-Cr	2.99×10^{-5}	0.372×10^{-1}
DASAPh-Mn	3.12×10^{-5}	0.383×10^{-1}

The magnetic moment was calculated using the equation (5)

$$\boldsymbol{\mu_{eff} = 2.828\sqrt{X_m T}} \quad (5)$$

Where, T = temperature in Kelvin, X_m = molar susceptibility.

The results of the magnetic moment and/or magnetic susceptibility measurement indicated very strongly an octahedral geometry around the central metal ion in all the metal complexes. It accounts for the occupation of two coordinating sites by chlorine out of six in making the octahedral environment. This is in accordance with result reported by (Liu *et al.*, 2003)

Morphological Studies of the Polymers

A Scanning Electron Microscope (SEM) was used to study the granule morphology of the representative resin. The native starch granules are oval in shaped; regular and truncated (Figure 2a). The granular shape was lost after oxidation by periodate to give lumps which are more closely packed and bigger (Figure 2b), similar to the DASAPh-metal chelate (Figure 2c) because of the breakage of the glucoside ring as indicated by the FT-IR results.

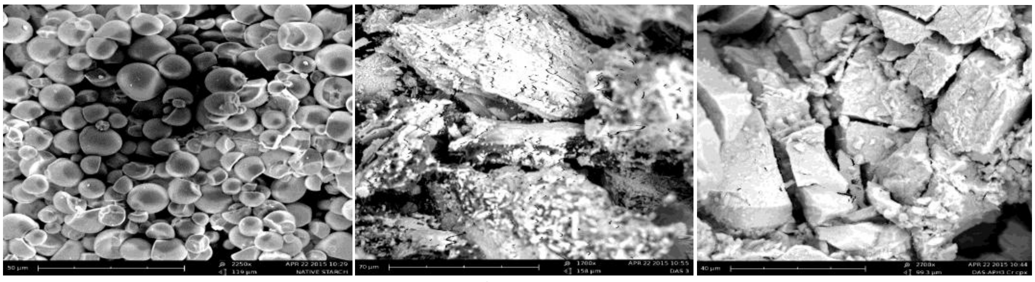


Figure 2; Scanning Electron Micrograph of (a) Native starch (b) Dialdehyde starch and (c) Dialdehyde starch aminophenol- metal chelate

The cleavage of the glucoside ring as indicated by FT-IR, gave an uneven surface with holes and pores (Figure 2b). The modified starch exhibited further fragmentation and irregular alignments of the particles probably due to the cleavage of the C_2 & C_3 bonds of the anhydrous glucose units of the starch polymer (Figure 2b). The micrographs of the polymer with adsorbed metal ions showed clear lumps indicating apparent changes that happen due to the presence of the chelated metal atoms in the polymer which resulted in cross linking of the polymer. The appearance of oval-shaped and truncated granules (Figure 2a) is in agreement with reports of Danjaji, *et al* (2000), and Odusanya, *et al* (2000), where the percentage of the starch determined the granule appearance. This however, changed with oxidation (Figure 2b) of the starch to give an aggregate of these lumps with few still scattered along the surface. The adsorption of metals onto the DASAPh (Figure 2c) gave very clear granules with very few oval-shaped of the few unreacted native cassava starch granules still present.

CONCLUSION

Modification of native cassava starch has been shown to improve its physicochemical properties. The modified and cross-linked polymers showed very good cross-linking ability. Their good thermal stability is an added advantage. This shows that chemical modification of native starch can help, in no small way to reduce water and environmental pollution, because of the ability of the modified starch to remove toxic heavy metals in aqueous solution, especially, in municipal and industrial wastewater treatments.

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