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Research Article

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Preparation and characterization of dialdehyde starch and its` cross-linking with copper (II) ion

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ABSTRACT

Starch derivatives were prepared using potassium periodate as oxidizing agent under mild condition and successfully reacted with copper(II) ion resulting in cross-linking of the dialdehyde part of the modified starch. The carbonyl content was determined and the starch, dialdehyde starch and the polymer copper II complex were characterized by conductivity test, solubility test, melting point, viscosity measurement and FT-IR spectral analysis.

Keywords: Dialdehyde Starch, Polymer metal complex, Oxidation, retrodegradation,

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INTRODUCTION

Modified starches are used practically in all starch applications, such as in food products as a thickening agent, stabilizer or emulsifier, in pharmaceuticals as a disintegrant, as binder in coated paper, in plastic and medicine. They are also used in many other applications [Anto *et al.*, 2006, Cavalho *et al.*, 2003]. Starch can easily melt and flow in the presence of plasticizers at temperatures of 90-180^{0}C under pressure and shear which allows it to be processed by injection, extrusion and blow molding. Re-crystallization (retro degradation) during plasticization of the starch is a major problem that has suppressed its widespread practical use as plastic because it easily become rigid and brittle during long term storage and thereby loses its utility over time [Zang *et al.*, 2009].

Several modified starches were prepared using different methods: physically, enzymatically, or chemically by treating native starch with various reagents, thereby changing the properties of the starch (Cavalho *et al.*, 2003). Esterification and etherification [Bogar et al., 2002] has been reported to improve the thermoplasticity and hydroplasticity of starch through the introduction of hydrophobic groups. However, these resulted in poor mechanical properties of the starch thereby suppressing its use as thermoplastic and biodegradable polymer applications [Delville et al., 2011].

Oxidation is another way of chemically modifying starch. Once the hydroxyl group of starch has been replaced with aldehyde group it shows greater hydrophobicity and the recrystallization inhibited [Zang et al 2009, Pedersen and Nielsen 2000]. Dialdehyde starch (DAS) prepared by periodic acid and periodate is the most valuable form of oxidized starch and can be used for several industrial applications as a food, in paper coating, in biomaterials, as wet-strength improver. However, the decomposition temperature of DAS drops due to the poor thermal stability of the aldehyde group, and so its glass transition temperature becomes higher than its decomposition temperature [Tokhadze *et al.*, 1975]. Zhang *et al.* (2009) reported a new method of modification of starch by oxidation of pea starch to aldehyde using sodium periodate under mild condition and subsequently acetalized the dialdehyde starch polymer with glycol to give Glycol-DAS. The modified starch was characterized by FT-IR, ^{1}H NMR, TGA, DSC and XRD. The influence of moisture absorption on the mechanical properties of modified starch polymer possesses improved water resistance. The tensile strength and elongation at break were 18.1-14.6 Mpa and 53-18% respectively.

On the other hand, coordination compounds are very important due to their role in biological and chemical systems in various ways. It has been observed that metal complex with appropriate ligands are chemically more significant and specific than the metal ions and the original ligand its` self. Currently the significance of metal ions in various biological systems has become important, as they are powerful inhibitor of enzymes as compared to un-complexed biological active compounds. Starch based coordination polymers are known to be completely biodegradable in the soil and water and can promote the degradation of non-biodegradable materials when blended or modified [Pan *et al.* 2003].

This paper present a preliminary investigation into modification of cassava starch by oxidation to dialdehyde starch using potassium periodate under mild conditions. The cassava dialdehyde starch was cross-linked with cupper (II) metal atom and the new starch derivatives were characterized using solubility test, conductivity measurement Viscosity measurement and FT-IR spectra studies.

EXPERIMENTAL SECTION

Materials

Dried cassava starch was purchased from Kurmi Market Kano, Potassium periodate, Hydrochloric acid (BDH), Sodium hydroxide (Across), Hydroxylamine hydrochloride (Sigma aldreich), Copper(II)chloride tetrahydrate ($CuCl_2.4H_2O$) (Acros), Dimethylsulfoxide (DMSO), Ethanol, Acetone, Calcium Chloride were obtained from Sigma-Aldriech and are of analytical grade. The FT-IR spectra were obtained from samples in KBr pellets using Shimazu.

The structure of the modified starches and the synthetic approach to the cross-liked polymer is illustrated in scheme 1. The detailed procedures are presented as follows

Preparation of dialdehyde starch

Exactly 37.9g of potassium periodate (0.5 molar ratio based on cassava starch) was dissolved completely in 400ml distilled water at room temperature 20 ^{0}C, followed by addition 60.0g of cassava starch with strong mechanical stirring. The reaction temperature was raised to 35 ^{0}C and the pH adjusted to 7.0. After 12 hours, the modified starch slurry was obtained. It was then filtered and the product was washed with 200ml warm distilled water five times. The powder was dried for 24 hours at 50 ^{0}C in an oven.

Measurement of the carbonyl content by titration method

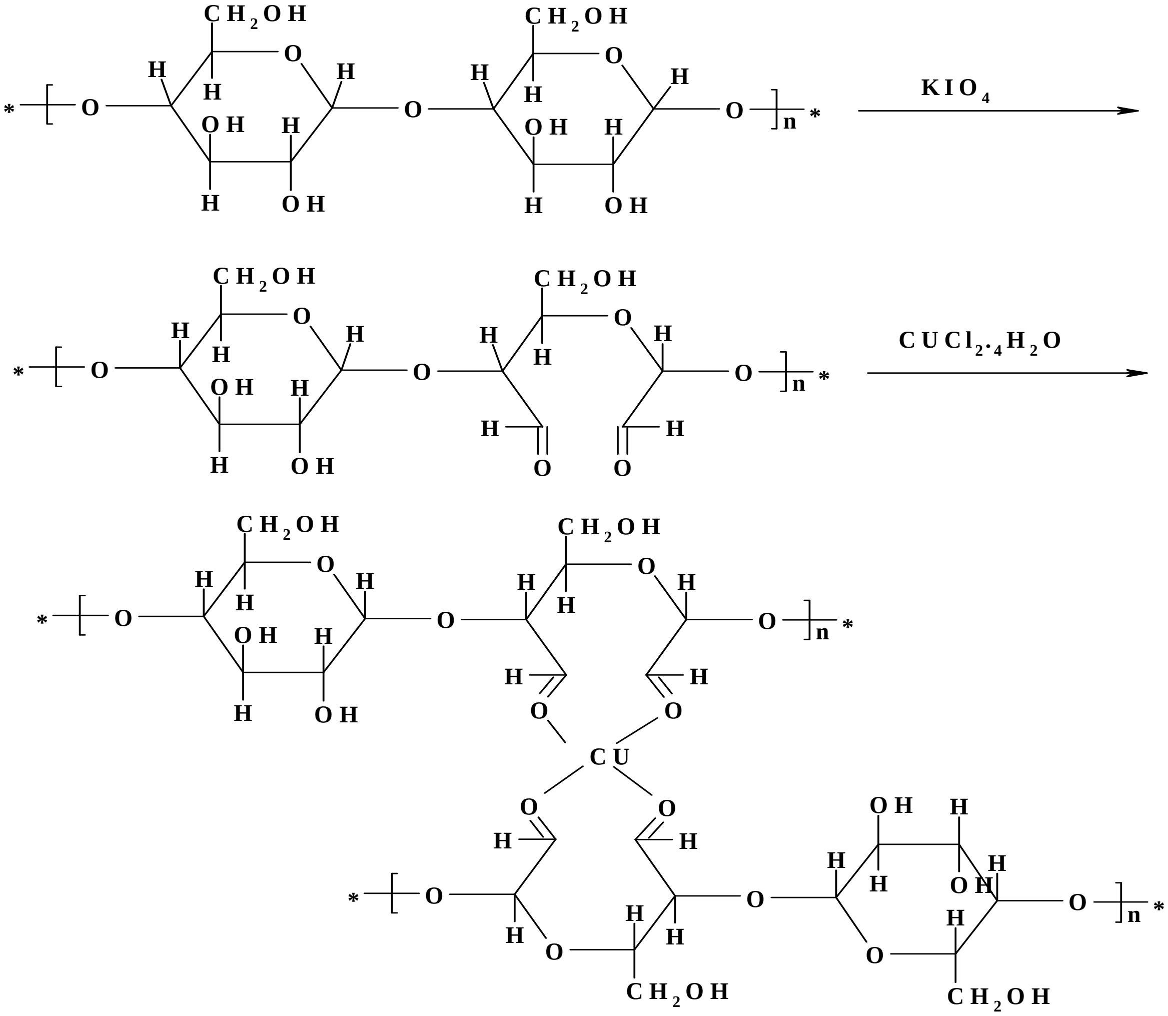
The carbonyl content of the dialdehyde cassava starches were determined according to the method described in the literature (Zhang *et al. 200*9). A dried sample (1.0g) was slurred in water (300ml) and heated to completely dissolve. The cooled solutions were adjusted to pH 3.2 with 0.118M HCl, and then 60.0ml of hydroxylamine hydrochloride (HMH) solutions was added (HMH 50.0g ; 100ml 0.1 M NaOH diluted to 500ml). The solution were heated to 40^{o}C in an oven for 4 hours and titrated rapidly to pH 3.2 with 0.118M HCl. Water was used as blank and sample was run three times and the coefficient of variation was 2%. The carbonyl content was calculated by the following equation.

$$CHO\% = 0.118 \times 0.028 \times (V_{control} - V_{sample}) \times 100\%$$

Where, $V_{control}$ is the volume of HCl consumed by water (the control), V_{sample} is the volume of HCl consumed by a sample (Zhang *et al.,* 2007).

Synthesis of Polymer-Metal Complex

Scheme **1** illustrates the synthetic route to the dialdehyde starch and the cross-link starch copper II metal complex. The copper II metal complex of DAS was prepared by using molar ratio (1:1) of DAS and the copper metal salt. A typical procedure for preparation of the copper (II) complex was carried out as follows: Exactly 2.22gm (0.01 mol) of DAS was dissolved in minimum quantity (25ml) of hot DMSO and 1.705g (0.01 mol) of Cu(II) salt was dissolved in DMSO (20ml) separately. Both solutions were filtered and mixed in hot condition with stirring. Then the reaction mixture was stirred at 60^{o}C for 4 hours. A brown coloured crystal product was obtained which was re-precipitated in distilled water. Finally, the product was filtered, washed with alcohol, acetone and re-crystallized from DMSO and dried in a vacuum desiccators on calcium chloride, yield 48.25% [Malik et al. 2009].



Scheme 1: Synthetic route to the cross-link polymer

Solubility test

Modified starch (DAS) and DAS-metal complex were tested for their solubilities in various common solvents by dissolving the sample in each individual solvent at room temperature (Table 3).

Measurement of viscosity

The intrinsic viscosity of the dialdehyde starch and cross link starch-cupper metal complex were determined using a capillary viscometer (Ubbelohde-type) in DMSO as solvent at temperature 25.0±0.2 ^{0}C and the concentration range of 0.2 to 1.0mg/ml.

RESULTS AND DISCUSSION

Modified starches are very vital as some are used to cure some diseases and also used as a food. It's important to determine the carbonyl content so as to cross-link the polymer with metal ions to obtain new material in order to increase its biological activity.

Table 1: Results of Titration

Burrete reading	Rough reading (cm^3)	1st reading (cm^3)	2nd reading (cm^3)
Final	2.00	4.50	6.50
Initial	0.00	2.00	4.50
Vol. of acid used	2.00	2.50	2.00

Average value of acid used = $\frac{2.5+2.0}{2}$ = 2.25cm^3

CHO% = 0.118 X 0.028 X (50 – 2.25) X 100

CHO% = 0.118 X 0.028 X 47.75 X 100

CHO% = 15.7766%

From the titration result above (table 1) suggested very low carbonyl content and this may be due to the fact that the potassium periodate was superfluous at this stage: it begins to oxidize the aldehyde to carboxylic acid and thus causing the carbonyl content decreases. When the molar ratio of potassium periodate to the cassava starch was higher than 1.0 the superfluous oxidant degraded the cassava starch and cause some of the dialdehyde starch to dissolve in water, resulting in decrease in carbonyl content [Petrucci *et al.*, 2007]. The carbonyl contents, which reflect the degree of oxidation, were expresses as number of carbonyl groups per 100 glucose units. The relationship of the molar ratio of potassium periodate to cassava starch to the carbonyl content was reported to be similar to its relationship to the yield [Zhang *et al.*, 2009].

Table 2: Some physical properties of the cassava starch, dialdehyde starch and the cross-link Polymer

Compound	Colour	Decomposition temperature
Cassava starch	White	200°C
Dialdehyde cassava starch	Purple	205°C
Cross-link polymer	Brown	267°C

The interaction of potassium periodate with cassava starch gave a purple coloured crystal decomposing at 205 °C and also the cross-linking of modified cassava starch with copper(II) chloride dihydrate gave a very stable cross-link polymer (complex) which decomposed at 276 °C, see table 2 above. The changes in colour observed and the decomposition temperature of the starches is a clear indication that the dialdehyde starch and the cross-link polymer has been successfully produced as complimented by the FT-IR result. The increase in the decomposition temperature of the modified starches exhibited an improved thermal stability which was mainly attributed to the cross-link polymer cupper metal complex and the reduced presence of HC=O groups in the samples [Yabuki *et al.*, 1997]. The thermal stability of the M-O bond is better than that of the HC=O (aldehyde group) bond and it is harder to oxidize at higher temperatures as a result the thermal stabilities of the cross-link polymer are better than those of the dialdehyde starch. Starch derivatives with higher thermal stabilities show favourable thermoplastic processing properties, especially in terms of preventing thermal decomposition, which is responsible for degrading mechanical properties [Prakasham *et al.*, 2007].

Table 3: Solubility of the cross-link polymer in various solvents

Solvent	Solubility
Water	SS
Methanol	SS
Ethanol	SS
DMSO	S
Acetonitrile	IS
Diethylether	IS
Hexane	IS
Chloroform	SS
DMF	S

S = soluble SS = slightly soluble IS= Insoluble

The prepared cross-link polymer (complex) was tested for solubility in water and common organic solvents. The Cross-link polymer is soluble in DMSO and DMF and, slightly soluble in water, methanol, chloroform and ethanol but, insoluble in acetonitrile, diethylether and hexane. The results are shown in the table 3.

Table 4: Conductivity of the cassava starch and its derivatives (DAS and cross-link) polymer

Compound	Specific conductance ($Ohm^{-1}cm^{-1}$)	Molar conductance ($Ohm^{-1}cm^{2}mol^{-1}$)
Cassava starch	32×10^{-6}	32
Dialdehyde cassava starch	38×10^{-6}	38
Cross-link polymer	46×10^{-6}	46

The molar conductivity values of the cassava starch, dialdehyde cassava starch and Cross-link polymer determined in 10^{-3}M DMSO is 32, 38 and 46 $ohm^{-1}cm^{2}mol^{-1}$ respectively indicating low values for the starch polymer, dialdehyde starch and the cross-link polymer. This is however, consistent with molar conductivity of non-electrolyte [Pedersen and Nielsen, 2000, Ray, 2001] and the result presented in table 4.

The FT-IR spectra of the compounds

For cassava starch a stretching vibration at 1089 cm^{-1} which is assigned to cyclic ether group of glucose molecule and stretching vibration at 3332cm^{-1} is assigned to hydroxyl group while stretching vibration at 2927 cm^{-1} to -CH_2- group [Zhang *et al.,* 2009]. For dialdehyde starch: a sharp band at 2923cm^{-1} is shown which is a characteristic of the -CH_2- stretching vibration and an intense band at 3385$cm^{-1}$is present which is assigned to deformation vibration of hydroxyl group in water [Zhang *et al.,* 2009] in the finger print there is discernible absorption at 1029 cm^{-1} which is assigned to C-O bond stretching [Zhang *et al.,* 2009]. A new broad band appears 1643cm^{-1} which is not observed in cassava starch spectra and this stretching vibration is assign to C=O in aldehyde group while, the absorption at 1404 cm^{-1} can be attributed to C-H vibration (Table 5).

Table 5: Result of FT-IR spectra for the modified starch polymers

Functional groups	γ(O-H)	γ (C-O)	γ (C=O)	γ (M-O)	γ (-CH_2-)	γ (C-H)
Cassava starch	3332cm^{-1}	1089cm^{-1}	-	-	2927cm^{-1}	1327cm^{-1}
Dialdehyde cassava Starch	3385cm^{-1}	1029cm^{-1}	1643cm^{-1}	-	2923cm^{-1}	1404cm^{-1}
Cross-linked polymer	3369cm^{-1}	1118cm^{-1}	-	615cm^{-1}	-	1413cm^{-1}

For cross-link polymer these bands were observed to have shift to lower and to a higher frequency due to γ (-OH) and γ (-C-O) respectively, in the complex indicating coordination of the dialdehyde starch to the metal ions. However new absorption band were observed at 615cm^{-1} assigned to γ (-M-O) stretching vibration [Silverstein and Bassler, 1967] in the complex which confirmed the complexation of the copper metal atom with the dialdehyde modified starch.

The intrinsic viscosity of the cassava starch, dialdehyde starch and the cross-link polymer were found to be 1.24, 0.89 and 0.54 respectively. The intrinsic viscosity of the dialdehyde starch was found to decreased, when KIO_4 cleaved the C2-C3 bonds of the glucose units of cassava starch. It was reported that the molecular weight of the starch decreased even under mild oxidizing conditions and the degree of degradation depends on the degree of oxidation [Huang *et al.,* 2003]. The branch amylopectin has a higher molecular weight and is easily oxidized by potassium periodate [Zhang *et al.,* 2009], which causes the molecular weight and intrinsic viscosity of the dialdehyde starch to decline drastically. When all the amylopectin has been oxidized, oxidation of the amylose content commences resulting in a slight decrease in the average molecular weight and the intrinsic viscosity of the dialdehyde starch.

CONCLUSION

Dialdehyde starch (DAS) with different carbonyl contents were prepared by the oxidation of cassava starch using potassium periodate as an oxidant under mild conditions. The cross-linked polymer (polymer/metal complex) was soluble in DMSO and DMF and, insoluble in water and other common organic solvents. Cross-linking of the starch polymer with transition metal can obviously improved the thermal stability of the modified cassava starches. It is therefore, important to prepare and study the cross-link polymer complexes of all the transition atoms.

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