Lima Bean Starch-Based Hydrogels

A.O. Oladebeye[a*], J.E. Imanah[a], O.I. Bakare[b] and A.A. Oladebeye[c]

[a]*Polymer Technology Department, Auchi Polytechnic, Auchi.*
[b]*Rubber Research Institute of Nigeria, Iyanomo, Benin-City.*
[c]*Food Technology Department, Auchi Polytechnic, Auchi*
*folabeye@yahoo.com, +234-803-3620-279

ABSTRACT

Hydrogels were prepared by crosslinking native lima bean starch and polyvinyl alcohol (PVA) with glutaraldehyde (GA) at varying proportions in an acidic medium. The native starch (N-LBS) and hydrogels (L-GA (low glutaraldehyde) and H-GA (high glutaraldehyde)) were examined for their water absorption capacity (WAC), swelling capacity, solubility, FTIR spectra and X-ray diffraction patterns. The hydrogels possessed higher WAC and swelling capacity than the native starch whereas an opposite trend was observed for their solubility values. The higher the GA proportion, the higher their WAC and swelling capacity, but the lower their solubility. There were indications of ether (C–O) groups and acetal rings (C–O–C) at 1023.53–1112.51 cm^{-1} bands. Absorption bands of O–H groups were observed. The crystals of N-LBS, L-GA and H-GA were classified as C_B-type, C_A-type and C_B-type patterns respectively.

INTRODUCTION

Starch is a versatile biopolymer that has found numerous applications in many industries other than food[1]. The major botanical sources of are cereals, roots and tubers while the minor sources are legumes[2]. Numerous polymer products have been developed owing to great expansion of starch use and utility[3]. The development of starch-based materials that can minimise the impact of chemicals on the environment as well as looking for alternatives to depleting petrochemical resources is on the high trend[4]. Starch-based hydrogels are three-dimensional network developed for short-life, disposable and specific applications[5, 6]. They are hydrophilic, and have been widely applied as drug delivery systems, bone cements, water absorbents, wound dressing, and as removal agents for toxic heavy metal ions. The structural integrity of hydrogels depends on cross-links established between the polymer chains, by chemical bonds and physical interactions[7]. Since the use of hydrogels is increasing, considerable efforts have been made in order to develop new hydrogels from a variety of synthetic and natural materials[8].

This present work focuses on the preparation of starch-based hydrogels by blending lima bean starch and polyvinyl alcohol (PVA) with glutaraldehyde (GA)

in an acidic medium of HCl. Starch and PVA are hydrophilic polymers, which are crosslinked with GA for improved swelling capacity and stability in aqueous systems. The use of glutaraldehyde as crosslinking agent for preparing bio-based hydrogels, such as chitosan, guargum, sodium alginate, collagen, alginate-guargum and Kappa carageenans has been reported[7]. To our knowledge, there is no study of preparing of hydrogels by blending lima bean starch and PVA by chemical crosslinking with glutaraldehyde and hydrogen chloride as the reaction catalyst. In this present work, the effects of varying amounts of GA and reaction time on the gelling behaviours of the hydrogels were studied.

MATERIALS AND METHODS

Materials

Lima beans (*Phaseolus lunatus*) were commercially purchased at Jattu Market, Etsako-West Local Government Area, Jattu, Edo State, Nigeria. Glutaraldehyde (GA), polyvinyl alcohol (PVA), hydrochloric acid (HCl) and ethanol used were commercially purchased and were analar grade.

Isolation of Native Starch

The native starch of lima bean was isolated, using the method described by Oladebeye et al.[1], which is illustrated in Fig. 1.

Synthesis of Hydrogel

The method of Carvalho et al.[7] was adopted for the preparation of lima bean starch/PVA/GA hydrogels with some modifications. A pre-weighed amount of PVA (5 g) was dissolved in 50 ml distilled water with constant stirring at 100^{o}C for 30 min to obtain a uniform dispersion. Certain amount of the dispersion of PVA (50 ml) was added to a known amount of lima bean starch (5% w/v) in a 250 ml jar (25%) followed by 1 ml of GA and 1 ml of 0.1 M HCl on a hot platform of 100^{o}C at constant stirring of 160 rpm for 60 min. The resulting gel was allowed to cool and later dispersed in 100 ml ethanol overnight. The wet gel was dried in the oven at a low temperature of 55±1^{o}C. The dried crisps were ground to fine particle size using mesh 250 μm. The procedure was repeated with 2 ml of GA at reaction time of 120 min (Table 1). The hydrogel samples were labelled as L-GA (low glutaraldehyde) and H-GA (high glutaraldehyde) hydrogels.

Methods

Water Absorption Capacity (WAC)

One gram each of the native starch and hydrogel samples was dispersed in 10 ml of distilled water and stirred for 30s. The dispersions were allowed to stand for 30 min, centrifuged at 2000 rpm for 30 min and the volume of the supernatant measured. The density of distilled water was taken to be 1 g/ml.

$$\% \text{ WAC} = \frac{\text{Weight of water absorbed}}{\text{Weight of sample}} \times 100$$

Swelling Capacity and Solubility

Swelling power and solubility of the starches were determined by adopting the standard chemical method described by Leach *et al.*[9] with some modifications. 100 mg of the starch sample was quantitatively and accurately weighted into a clean dried test tube and re-weighed as W_1. The starch sample was dispersed in 50 ml distilled

water and mixed using vortex mixer. The resulting slurry was heated at 70^{o}C for 45 min in a water-bath.

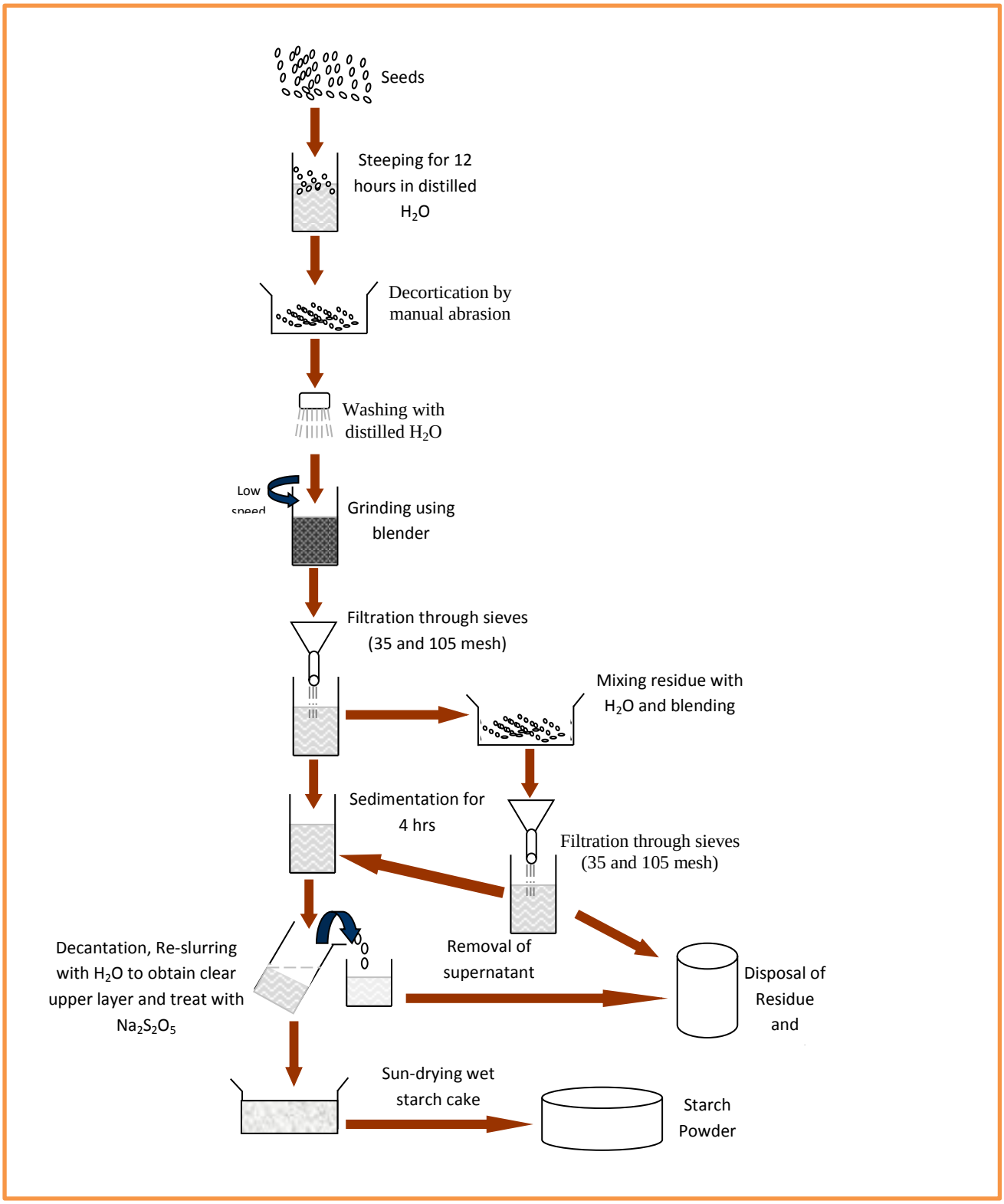


Figure 1: Isolation of lima bean starch

The mixture was cooled to 28±2^{o}C and centrifuged at 2200 rpm for 15 min to separate the gel and supernatant. The supernatant was removed and poured in a dish for solubility determination. The weight of the swollen sediment was determined (W_2).

The supernatant was dried to a constant weight in an air-oven at 100^{o}C for 4 hours.

$$\text{Swelling Power (g/g)} = \frac{W_2 - W_1}{\text{Weight of Sample}}$$

$$\text{Solubility(\%)} = \frac{\text{Total Weight of Solubles}}{\text{Weight of Sample}} \times 100$$

Fourier-Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectra of the samples were obtained in the range of 400 to 4000 cm^{-1} using a Jasco-FTIR spectrophotometer (Jasco, Essex, UK) by the KBr disc method. Pellets were prepared using a pressure of 14,000 pound for 2 minutes.

X-ray Diffraction Patterns

The x-ray diffraction studies were carried out using a Siemens D5000 X-ray Powder Diffractometer (20^{o} Geometry, Madison, USA). The starch samples were equilibrated with distilled water in a dessicator of 48 h before determination to improve resolution of the x-ray diffractogram pattern. The fine samples were filled into a sample holder and packed as densely as possible. The finished surface was smoother and flushed. The samples were mounted into a X–ray diffractometer and copper Kα, 2λ (λ = 1.540 μm and 1.544 Å; 40 KV; 30 mA) was generated to determine x-ray pattern. The scan was made from a diffraction angle (2θ) of 10 to 100^{o} at 0.06 step size with a count time of 59.69 s. From the resulting x-ray patterns, peak positions were identified using the instrument's software and these peak positions were used to determine the crystalline natures of the starch samples[10].

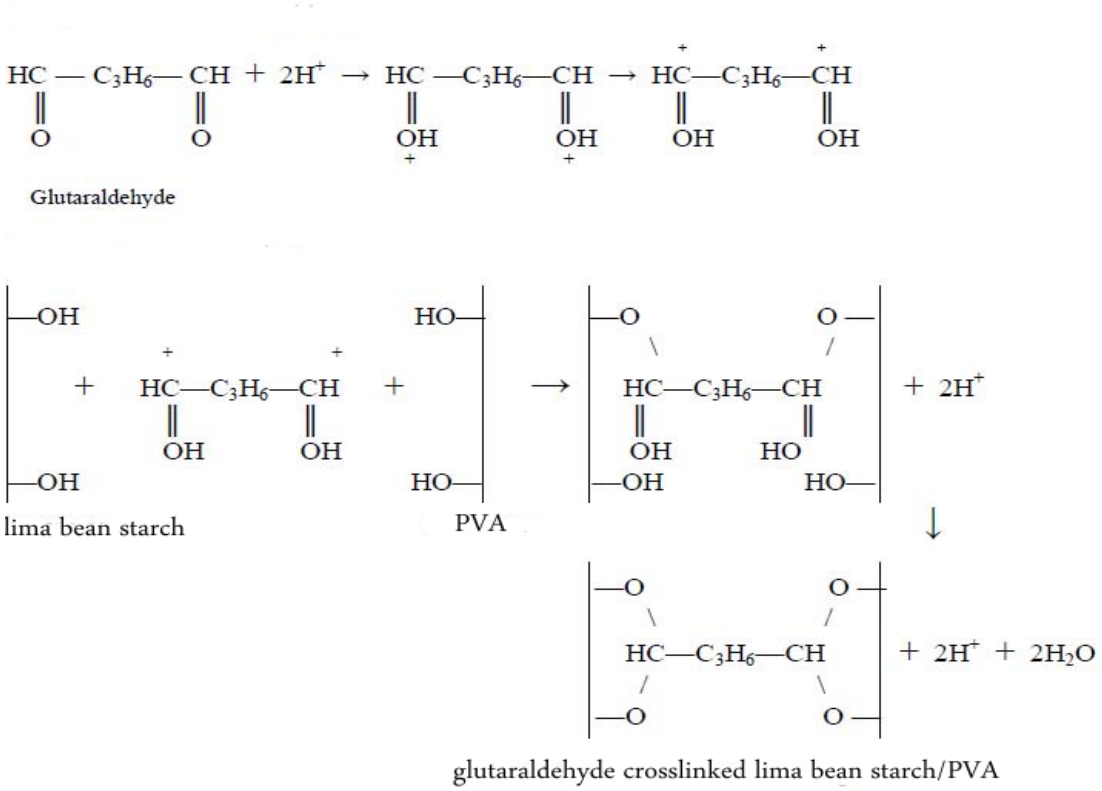


Figure 2: Proposed mechanism of lima bean starch-based hydrogel

RESULTS AND DISCUSSION

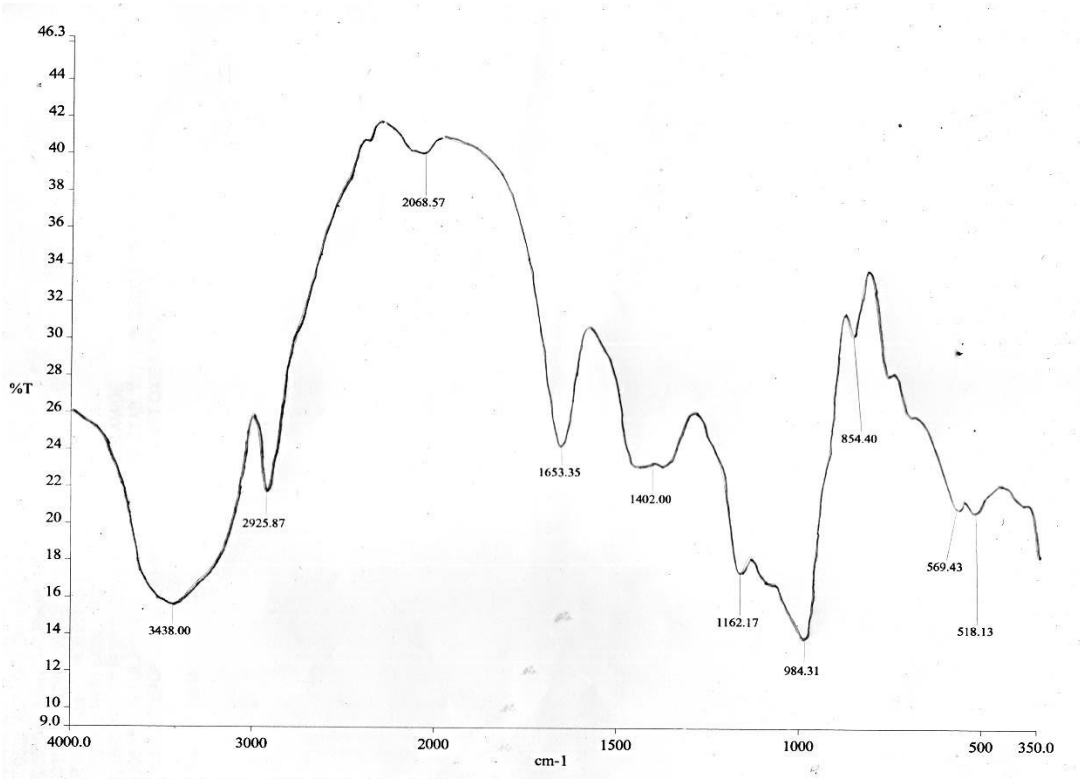
Water Absorption Capacity, Swelling Capacity and Solubility

Water absorption capacity (WAC), a measure of degree of engagement of the starch molecules to form hydrogen and covalent bonds between starch chains and the degree of availability of water binding sites among the polymer network, varies among the samples (Table 1).

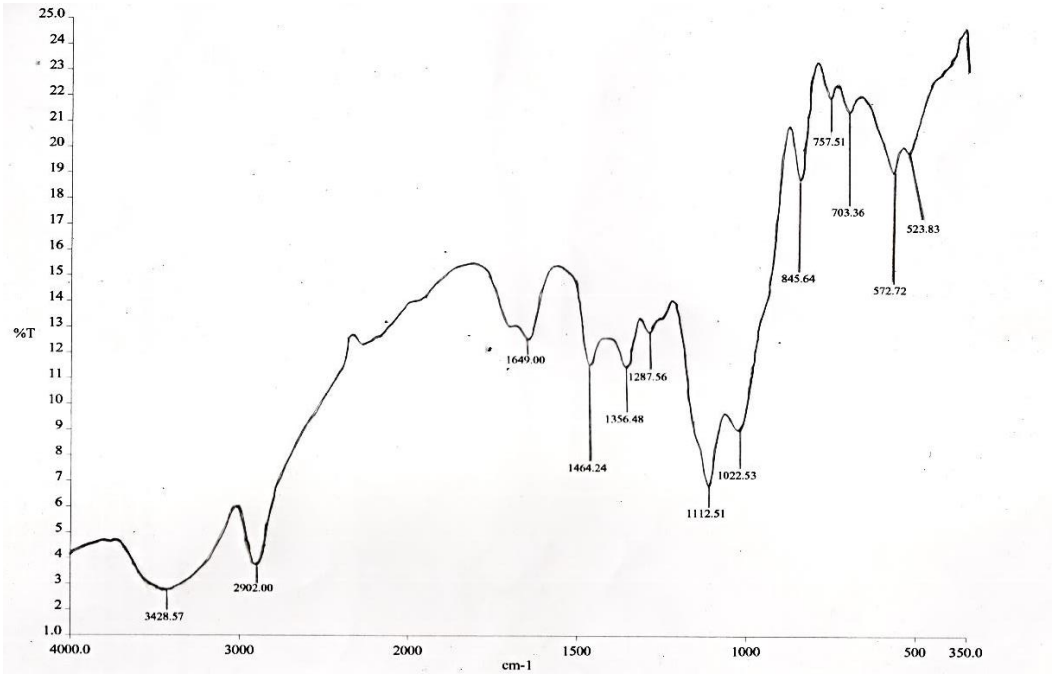
Table 1: Water absorption capacity, swelling power and solubility of the samples

Sample	Water Absorption Capacity (%)	Swelling Power (g/g)	Solubility (%)
N-LBS	149	2.80	19.00
L-GA	190	4.30	18.00
H-GA	200	4.33	17.00

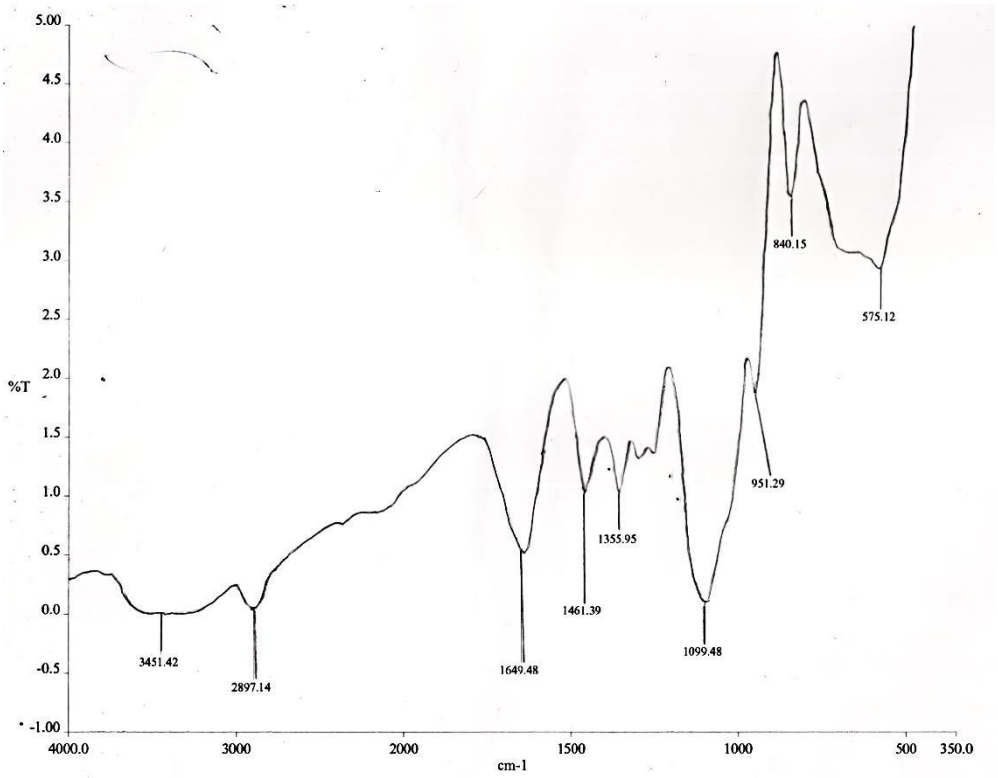
N-LBS = native lima bean starch, L-GA = low glutaraldehyde hydrogel, H-GA = high glutaraldehyde hydrogel


%T
cm-1
3438.00
2925.87
2068.57
1653.35
1402.00
1162.17
984.31
854.40
569.43
518.13

(a)


%T
cm-1
3428.57
2902.00
1649.00
1464.24
1356.48
1287.56
1112.51
1022.53
845.64
757.51
703.36
572.72
523.83

(b)



(c)

Figure 3: FTIR spectra of: (a) N-LBS, (b) L-GA and (c) H-GA

The percentage water absorption capacities of the hydrogels are higher than the value obtained for the native lima bean starch. These differences could be attributed to the tendency of glutaraldehyde (GA) to disrupt the inter- and intra- molecular hydrogen bonding that binds the hydroxyl groups in the starch-PVA chains by creating more water binding sites, which result in increase in hydrophilicity of the hydrogel molecules. In addition, the capacity of H-GA (high GA hydrogel) molecules to absorb water (200%) is higher than the value obtained for L-GA (low GA hydrogel).

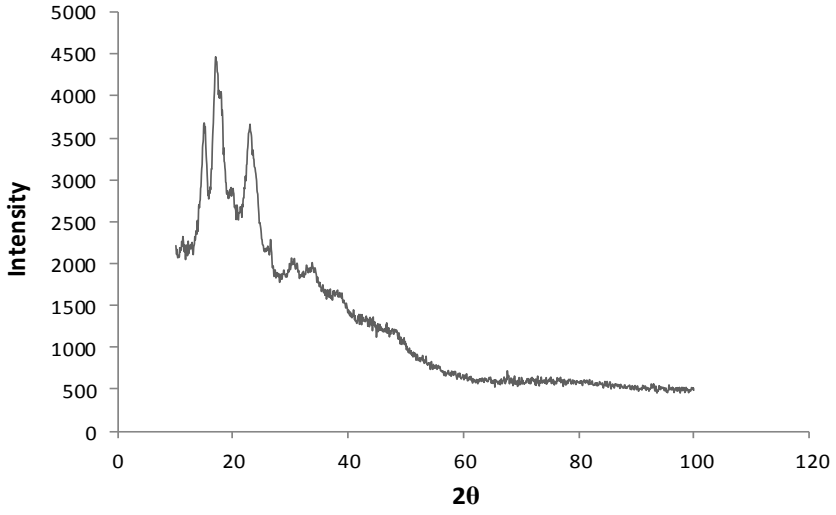
This implies that increase in glutaraldehyde proportion and reaction time enhances the water absorption capacity of the hydrogels. Invariably, hydrogels possess higher water absorption capacity than the native starch.

From Table 1, the hydrogels possess higher values swelling capacity than the native starch with progressive increase as glutaraldehyde proportion increases. An opposite trend is observed for the solubility values of the samples. The possible formation of acetal rings and ether groups as a result of crosslinking with glutaraldehyde, as shown in Figure 2, could result in subsequent lowering of the hydroxyl groups, followed by increase in hydrophilicity of the hydrogels.

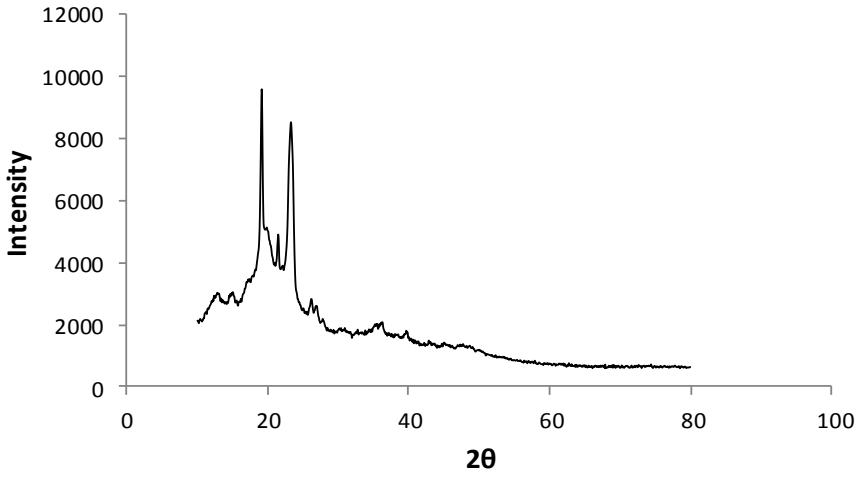
FTIR Spectra

The FTIR spectra of the native starch, L-GA and H-GA are depicted in Fig. 3. The spectra broad band observed at 984.31 $cm^{-1}$is an indication of hydrogen

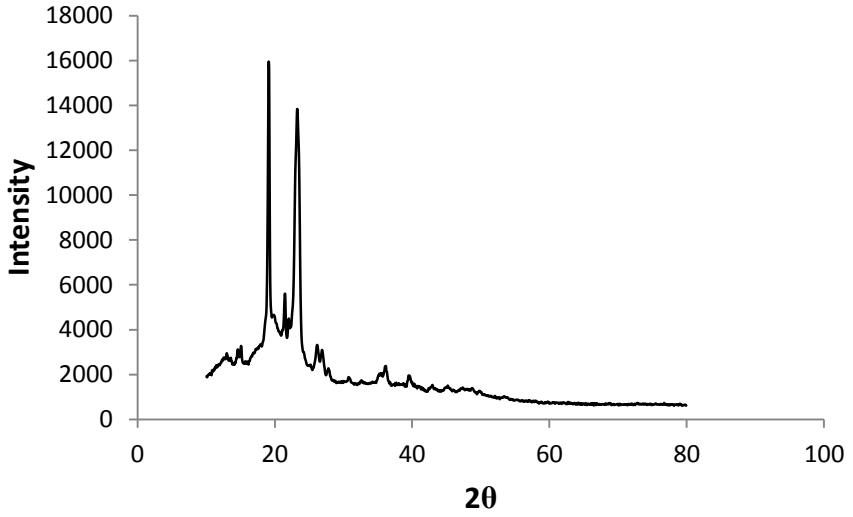
bonding of the hydroxyl group at C6 of the native starch[11]. Likewise, broad band at 3428.57 cm^{-1} is shown by the native lima bean starch, which indicates the hydrogen bonded hydroxyl groups that contribute to the vibrational stretch, associated with inter- and intra- molecular bound hydroxyl group, having polymeric association that makes up the gross starch three-dimensional structure. In addition, the C–H broad alkyl stretching is observed at 2925.87 cm^{-1} band for the native starch. The FTIR spectra of L-GA and H-GA show the presence of very strong absorption band at 1023.53 – 1112.51 cm^{-1} indicative of C–O stretching, which can be attributed to the ether (C–O) and acetal ring (C–O–C) bands, formed by the crosslinking reaction of GA with starch/PVA chains. There are no new peaks of free C=O groups in the spectra of the hydrogels. This implies that al the carbonyl groups of glutaraldehyde have been used up for crosslinking[12]. Strong absorption bands of hydroxyl group (O–H) are observed at 3428.57 cm^{-1} and 3451.42 cm^{-1} for L-GA and H-GA respectively. These O–H groups are termed free hydroxyl groups in the hydrogels. However, these hydroxyl groups bands observed in the hydrogels are more reduced than the bands observed for the native starch. Weaker hydrogen bonding in crosslinked PVA due to reduction in hydroxyl groups have been adduced to acetal formation in the hydrogels[13]. This could be adduced to reduced interaction between the glucan chains of the starch, resulting in the disruption of inter- and intra- molecular hydrogen bonds. This, in no doubts, could result in increase in hydrophilicity of the hydrogel molecules compared to the native starch. This observation is in agreement with the results of water absorption capacity (WAC) obtained for the native starch and the hydrogel samples in this current research work (Table 1).



(a)



(b)



(c)

Figure 4: XRD Patterns of: (a) N-LBS, (b) L-GA and (c) H-GA

The swelling power of starches is of great significance in tablet and capsule formulations, as it is believed that disintegrants work through a swelling and wicking action[14]. As a result, hydrogels studied in present work, would be expected to release the active pharmaceutical ingredient from its compacts at a faster rate, when used as a disintegrant in drug delivery system.

X-ray Patterns

X–ray diffraction peaks obtained for the native starches appear at 15.15^{o}, 17.15^{o} and 18.11^{o} 2θ, which correspond to interplanar d–spacing of 5.85 Å, 5.17 Å and 4.90 Å respectively (Figure 4). These data are in agreement with previous observations for lima bean starch by Oladebeye et al.[15]. The crystals of lima bean are mixes of A- and B-polymorphs with B-polymorph more predominant. Hence, the native starch is classified as C_B-type of crystallinity. L-GA exhibits diffraction peaks at 19.16^{o}, 20.00^{o} and

23.55^{o} 2θ, which correspond to 4.63 Å, 4.44 Å and 3.78 Å respectively. The peak at 23.55^{o} 2θ is characteristic of C-type pattern, which is a mix of A- and B-polymorphs. In addition, the appearance of a weak peak at 20.00^{o} 2θ, which is characteristic of A-type patterns shows that the crystals of L-GA can be classified as C_A-type patterns (Figure 4). The crystals of H-GA exhibit diffraction peaks at 19.12^{o}, 21.46^{o} and 23.53^{o} 2θ, which correspond to 4.64 Å, 4.14 Å and 3.78 Å respectively. Likewise, the crystals of H-GA belong to C-type patterns with a slight transformation to weak peak at 21.46^{o} 2θ, which is characteristic of B-type polymorph. H-GA crystals are, therefore, classified as C_B-type patterns. These differences can be adduced to the effect of glutaraldehyde on the amylose/amylopectin chains of the starch matrix of the hydrogels on which the crystalline pattern depends.

CONCLUSION

Hydrogels were successfully prepared from the native lima bean starch and their properties were strongly affected by glutaraldehyde proportions. FTIR spectra confirmed the formation of new peaks of acetal rings and ether groups, which were indicative of crosslinking between glutaraldehyde and starch/PVA chains. Swelling capacity and water absorption capacity increased with increase in glutaraldehyde proportion and reaction time, with corresponding decrease in solubility values. The native starch, L-GA and H-GA exhibited C_B-type, C_A-type and C_B-type patterns respectively. The hydrogels prepared and examined in this present research work could be potential disintegrants in drug delivery systems, and in the production of diapers.

REFERENCES

1. Oladebeye, A.O., Oshodi, A.A., Amoo, I.A. and Karim, A.A. (2013a). Hydroxypropyl derivatives of legume starches: Functional, rheological and thermal properties, Starch/Starke 2013, 65, 762–772.

2. Karim, A.A., Norziah, M.H. and Seow, C.C. (2000). Methods for the study of starch retrogradation: A review. Food Chemistry, 71, 9–36.

3. Shannon, J. C.; Garwood, D. L. and Boyer, C. D. (2009). Genetics and Physiology of Starch Development: Chapter 3. In BeMiller, J. and Whistler, R. (Ed). Starch: Chemistry and Technology (3^{rd} ed), Elsevier, Amsterdam, pp. 24–25.

4. Cadar, O., Paul, M., Roman, C., Miclean, M., Majdik, C. (2012). Biodegradation of poly(lactic acid) and (lactic acid-ethylene-malonic or succinic acid) copolymers under controlled composting conditions in a laboratory system. Polym. Degrad. Stab., 97, 354–357.

5. Hennink, W.E. and van Nostrum, C.F. (2002). Novel crosslinking methods to design hydrogels. Adv. Drug Deliv. Rev., 54, 13–36.

6. Nguyen, K.T. and West, J.L. (2002). Photopolymerizable hydrogels for tissue engineering applications. Biomaterials, 23, 4307–4314.

7. Carvalho, J., Gonçalves, C., Gil, A.M. and Gama, F.M. (2007). Production and characterization of a new dextrin based hydrogel. European Polymer Journal, 43, 3050–3059.

8. Drury, J.L. and Mooney, D.J. (2003). Hydrogels for tissue engineering: scaffold variables and applications. Biomaterials, 24, 4337–4351.

9. Leach, H.W., McCowen, L.D. and Schoch, T.J. (1959). Structure of the starch granule I. Swelling and solubility patterns of various starches. Cereal Chemistry, 36, 534–544.

10. Jayakody, L., Hoover, R., Liu, Q. and Donner, E. (2007). Studies on tuber starches. II. Molecular structure, composition and physicochemical properties of yam (*Dioscorea spp*) starches grown in Sri Lanka. Carbohydrate Polymers, 69:148–163.

11. Van Soest, J.J.C., Tournois, V.H., De Wit, D. and Vliegenthart, J.F.C. (1995). Short–range structure in (partially) crystalline potato starch determined with attenuated total reflectance Fourier-Transform IR spectroscopy. Carbohydrate Research, 279, 201–214.

12. Patel, A.R. and Vavia, P.R. (2010). Evaluation of synthesised crosslinked polyvinyl alcohol as potential disintegrant. Journal of Pharmaceutical Science, 13(2), 114-127.

13. Lavin, E. and Snelgrove, L. (1983). Vinyl polymers. In: Othmer, K. (Ed.), Encyclopedia of Chemical Technology, John Wiley, New York, pp 808–821.

14. Adebayo, A.S. and Itiola, O.A. (1998). Evaluation of breadfruit and cocoyam starches as exodisintegrants in a paracetamol tablet formulation. Pharmacy Pharmacology Communications, 4, 385–389.

15. Oladebeye, A.O., Oshodi, A.A., Amoo, I.A. and Karim, A.A. (2013b). Morphology, X-ray diffraction and solubility of underutilized legume starch nanocrystals, International Journal of Science and Research, 2(3), 497–503.