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Development and Characterization of Composite Films using Collagen Hydrolysate Extracted from Chromed Leather Wastes

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ABSTRACT

Discharges of huge quantities of leather solid wastes by leather industries and the increased use of synthetic packaging films have raised serious concerns on account of their environmental impacts. The paper focus on the development and characterization of potential environmentally friendly composite films using collagen hydrolysate (CH) extracted from chromed leather solid wastes and starch isolated from mango seed embryo, in order to assess the feasibility of producing polymeric materials suitable for applications in packaging and wrapping purposes.

Keywords: *collagen hydrolysate, starch, composite films, chromed leather wastes.*

INTRODUCTION

Leather industry has been categorized as one of the highly polluting industries and there are concerns that leather-making activity can have an adverse impact on the environment. The global production of about 24 billion m2 of leather by 2005 presents a considerable challenge to the industry considering the harmful nature of some of the chemicals used in leather processing. The tannery effluents are characterized by high contents of dissolved, suspended organic and inorganic solids giving rise to high oxygen demand and potentially toxic metal salts and chromium metal ion. The disagreeable odour emanating from the decomposition of proteinous waste material and the presence of sulphide, ammonia and other volatile organic compounds are also associated with tanning activities [1].

Solid wastes generated in leather industries contribute mainly skin trimmings, Keratin wastes, fleshing wastes, chrome shaving wastes and buffing wastes. It constitutes protein as the main component. If these protein and other chemicals, which are present in the chemical treated protein, are not utilized properly it will pose hazardous pollution problem to the environment [1].

Tanneries apply chrome (III) based processes in tanning and this is still the most efficient method of tanning and the one that provides the best qualities to the final products. As a way of reducing the consumption of raw materials, energy and water, a circular economy model in the leather industry has been tested. It aims to reduce, reuse, recycle and recover tannery waste in the different operation stages of leather processing. However, in a tannery, for each 1000 kg of hides or skins processed, about 250 kg of chrome leather waste and at least 500 kg of total solid waste are produced. This industry generates about 4 million tons of waste per year worldwide [2].

Using the products obtained from chrome leather waste (CLW) in other industries apart from tanneries is also a feasible and sustainable alternative. Researchers have used CLW to produce adsorbents for wastewater treatment. Alternatives aiming at the reuse of CLW have been studied. Some examples are the production of pigments, carbon ferrochromium alloy, basic chromium sulphate and polymeric microcapsules. Also, hydrolysis has been used to extract protein from CLW. Hydrolysis of CLW consists in reversing the reaction of the tanning agent (chromium) with the collagen which is responsible for the leather stability. The high breaking of the chromium collagen bonds is essential to the process. Hydrolysis can be performed in acid media, alkaline media or by enzymes. When performed in alkaline media, hydrolysis produces a protein (collagen hydrolysate or gelatin) in aqueous solution and a solid cake- rich in chromium. Although collagen hydrolysate extraction from CLW has been already studied, its later applications have to be more explored since new fractions has been suggested to be used in leather production or animal feed [3-6].

Not only management of wastes in industries like tanneries is an environmental issue to be widely discussed. The extensive employment of synthetic has encouraged researchers to find alternative renewable sources. Thermoplastic starch, for example, requires 68 % less energy than polymers produced from petroleum. It also has a lower cost when it comes to raw material price and emits lower rate of CO2 to the atmosphere during production process [2].

EXPERIMENTAL

Materials/Equipment

Chromed leather wastes (shavings, buffing dust and trimmings), Magnesium oxide (alkalinizing agent), Glycerol, Mango starch, Sodium hydroxide, hydrogen tetraoxosulphate (vi) acid, Boric acid, Stuart flask shaker (model No. 1291), Kjeldahl apparatus (Gallenhamp NKS 200 010H) and water vapour permeabilizer (Muver, 5011).

Extraction of Collagen Hydrolysate from Chromed Leather Wastes (CLW)

For collagen hydrolysate extraction, 50 g of CLW was weighed and mixed with 3 g of Magnesium Oxide (MgO) and 300 ml of water in a 500 ml conical flask and hydrolysis was carried out in a reciprocating shaker for 6 hrs at 70 o C.

After which the mixture was filtered and the filtrate which was rich in collagen hydrolysate was collected and stored in a refrigerator for subsequent use.

Characterisation of the CLW and Collagen Hydrolysate

pH: The pH for the chromed leather wastes before hydrolysis, and that of the extracted collagen hydrolysate after hydrolysis was determined using a pH meter according to ASTM D6657-2014.

Ash Content

Ash content was estimated by the measurement of the residue left after the combustion of 4 g of CLW and 10 ml of collagen hydrolysate in a crucible at 400 oC and the percentage of CLW and collagen hydrolysate were calculated relative to the number of samples combusted.

Moisture Content

Moisture content of CLW and Collagen hydrolysate was determined according to ASTM D3790-2012. 4 g of CLW and 10 ml of collagen hydrolysate was weighed into a crucible, heated with heating mantle under a specified condition (temperature of 85^{o}C at a time of 75mins for collagen hydrolysate and 5hrs for CLW), the samples were removed, reweighed. This was repeated until a constant weight was achieved and the loss of weight was used to calculate the moisture content of the samples.

Total Kjeldahl Nitrogen measurement

The macro Kjeldahl method followed by titration was used for Total Kjeldahl Nitrogen (TKN) determination, which was used as a measure of protein content in the collagen hydrolysate. The analysis was carried out according to SMEWW-4500N –B in collagen hydrolysate and ASTM D2868-2010 in CLW. 3 g of CLW and 10 ml of collagen hydrolysate were weighed into a digestion flask and then digested by heating it in the presence of a catalyst (copper) to speed up the reaction. Digestion converted the nitrogen in the samples into ammonia. After the digestion had been completed, the digestion flask was connected to the receiving flask through a tube. The respective solutions in the digestion flask were made alkaline by the addition of sodium hydroxide which converted the ammonium sulfate into ammonia gas. The ammonia gas formed was liberated from the solution and moved out of the digestion flask-which contained an excess of boric acid. The low pH of the solution in the receiving flask converted the ammonia gas into ammonium ion and also the boric acid to borate ion. The nitrogen content was then estimated by titration of the ammonium borate formed with a standard sulfuric acid, a methyl orange (indicator) was used to determine the end-point of the reaction. The TKN of the samples were determined with the following equation:

% N = (x moles/ 1000 cm^3) x ((v_s– v_b) cm^3/mg) x ((14g/moles) x 100),

Where: vs and vb = titration volumes of the respective samples and blank

14g is the molecular weight of nitrogen.

The nitrogen content was converted to protein content with the use of a conversion factor of 6.25 (equivalent to 0.16 g nitrogen per gram of protein).

This implies that: % protein = F (conversion factor) x %N.

Chrome content

Chromium in CLW was determined as chromic oxide through perchloric acid oxidation

followed by sodium thiosulphate titration according to ASTM D2807-2009. For chromium content in collagen hydrolysate, samples were prepared according to Standard Methods For Examination of Water and Wastewater (SMEWW) Method 3030-E and then analyzed by atomic spectroscopy according to SMEWW Method 3111-B.

Preparation of Polymeric Film

Samples of polymeric film were prepared by dispersing 3.5 g of starch in a 100 ml of dispersion media (collagen hydrolysate and distilled water) as shown in table 2.1 below. The solution for each sample was heated with a heating mantle at a temperature of 85 ^{o}C for 90 minutes under constant stirring until a gel is formed. The heating was stopped and the blend was cooled to room temperature and then was cast in a 10×4 cm glass plate covered with a mould releasing agent (mirror glaze). The cast film was allowed to dry in a dry air oven at a temperature of 30 ^{o}C.

Table 2.1. *Composition of the four films which was produced in duplicate.*

S/N	Sample	Solvents Used	Glycerol (g)
1.	A	Collagen hydrolysate	0.45
2.	B	Collagen hydrolysate	0.00
3.	C	Water	0.45
4.	D	Water	0.00

Testing of the Prepared Films

Hardness test

The sample was placed on a hard flat surface. The indenter for the instrument was then pressed into the sample making sure that is parallel to the surface. The hardness was read within one second. A minor load was applied to the sample which established a zero position. After the minor load, a major load was applied and then removed while the minor load was maintained. The difference in depth between the minor and the major loads determined the hardness. This was repeated thrice for each sample and an average of each was recorded. The hardness of the sample was measured by an indentor (ASTM D2240).

Water vapour permeability test

Samples of tanned leather were cut to the shape and diameter of the permeability cup, the surface of the various leather samples were covered with the films produced with different composition, clamped across the mouth the permeability cup filled with 15 ml of distilled water which contains a solid desiccant and was kept in a conditioned room. The air within the bottle was circulated by keeping the desiccant in motion. The cup was weighed periodically (after 30 mins) to determine the mass of vapour transmitted through the leather and absorbed by the desiccant.

$WVP=7369M/D^2T$, Where; M=Difference in the mass of the sample,

D = Diameter of the cup (34 mm)

T=Time of run in seconds

RESULTS AND DISCUSSION

Characterized CLW and Collagen Hydrolysate

Table 3.1.*Parameters of CLW and Collagen Hydrolysate*

S/N	Parameter	CLW	Collagen Hydrolysate
1.	pH	3.72	8.40
2.	Moisture(%)	53.35	98.00
3.	Ash(%)	8.2	14.8
4.	TKN(Mg/L)	14	2,140
5.	Cr_2O_5(%)	6.5594 (%)	0.1477 (Mg/L)
6.	TKN/Cr ratio	2.1	14,488.8
7	Protein yield (%)	87.5	13375

Table 3.1 shows the properties of the characterized chromed leather waste and the extracted collagen hydrolysate respectively. The pH of chromed leather waste was found to be 3.72 which is acidic, while that of the extracted collagen hydrolysate is 8.40, which is alkaline. This high pH value (i.e. 8.40) obtained for the collagen hydrolysate can be attributed to the alkalinizing agent magnesium oxide MgO that was employed during hydrolysis. The moisture

content of the chromed leather waste and the extracted collagen hydrolysate was 53.35 and 98.00 % respectively. The high moisture content of 98.00 % of the collagen hydrolysate can be attributed obviously to the fact that the collagen hydrolysate is in aqueous solution. It can also be seen from the results obtained that the extracted collagen hydrolysate had a relatively high ash content of 14.8 % when compared to that of the chromed leather waste which was found to be 8.2 %. This higher ash content seen in collagen hydrolysate could be attributed to the residues of the alkalinizing agent, MgO, used during hydrolysis of the chromed leather waste. The Total Kjeldahl Nitrogen (TKN) contents of the CLW and CH was measured to be 14 % and 2,140 Mg/L respectively. Also, the chromium content of the CLW is 6.5594 % while that of the CH is 0.1477 %. This reduction in chromium content of the CH could be an indication that chromium hydroxide precipitated more easily during hydrolysis. The TKN/Cr ratio of the CLW and that of the CH was 2.1 and 14,488.8 respectively. The relatively higher TKN/Cr ratio of the CH indicated the alkaline hydrolysis of the CLW using magnesium oxide at the specified conditions was effective in extracting collagen hydrolysate from the CLW. This also explains the higher protein yield of 13375.0 % for the collagen hydrolysate when compared to that of the chromed leather waste of 87.5 %. A total volume of 260 ml of collagen hydrolysate was extracted. It is important to note here that the reproducibility of collagen hydrolysate extraction depends on the characteristics of the chromed leather wastes employed in the process. Some slight differences can be found among CLWs due to the origin of raw hides and skins, and also because of the tanning process used [2].

Characterization of Produced Film

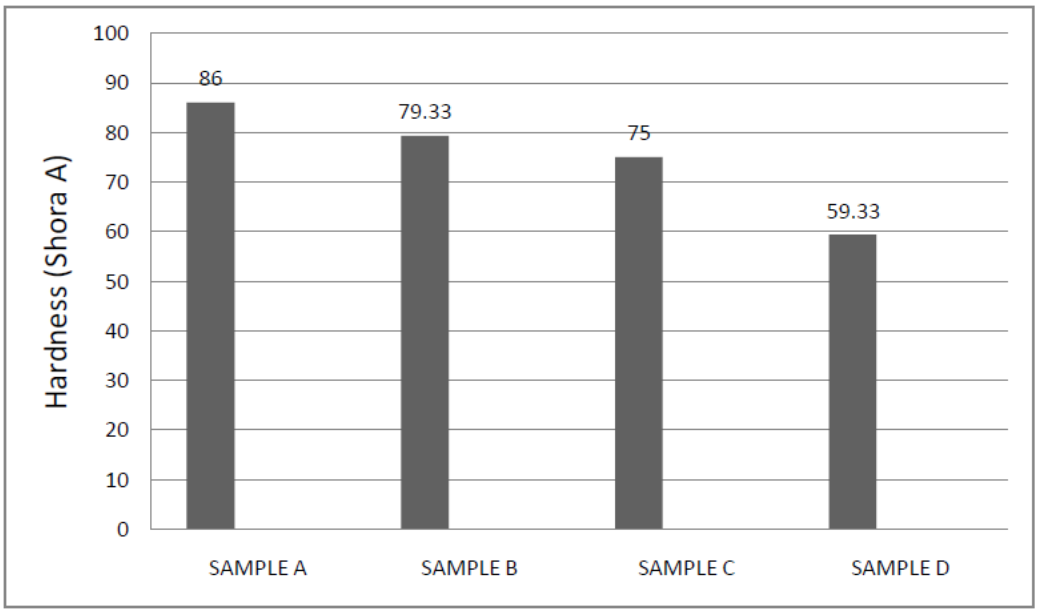

Fig 1.*A Chart Illustrating the Average Degree of Hardness of the Produced Film*

Figure 1 shows the results of the shore A hardness of the produced composite films. Generally, the shore A hardness values of the produced films decreased from sample A with a Shore A value of 86.00 to sample D with a shore A value of 59.33. Samples B and C have a shore A hardness values of 79.33 and 75.00 respectively. When compared on the basis of the type of solvents used, samples A and B which contained collagen hydrolysate as the solvent had a higher Shore A hardness values than that of samples C and D which contains distilled water as the solvent. This improvement in the shore A hardness of the films by the collagen hydrolysate could be due to the higher molecular weight that the collagen hydrolysate might have imparted the resulting film solution. Another basis of comparison is in the glycerol content. Sample A which contains 0.45 g of the glycerol has a higher Shore A hardness value than sample B with a glycerol content of 0.00 g. Similar results are also obtained for samples C and D, with sample C containing 0.45 g of the glycerol while sample D has 0.00 g glycerol content.

Figures 2 and 3 show the water vapour permeability of the films produced after 30 minutes and 1 hour respectively. From the

results of the two figures, it can be seen that the water vapour permeability of the sampled films increases with the length of time of the experiment. And for each time of 30 min and 1 hr, the water vapour permeability of the sampled films increased from 0.00004 Kg/mm^2.s and 0.00033 Kg/mm^2.s respectively for samples A to 0.00154 Kg/mm^2.s and 0.00208 Kg/mm^2.s respectively for the control samples. It, therefore, implies that the presence of collagen hydrolysate in the composition mixture improved the water vapour permeability of the films which is further enhanced by adding glycerol. This can be attributed obviously to the gelling property of collagen hydrolysates.

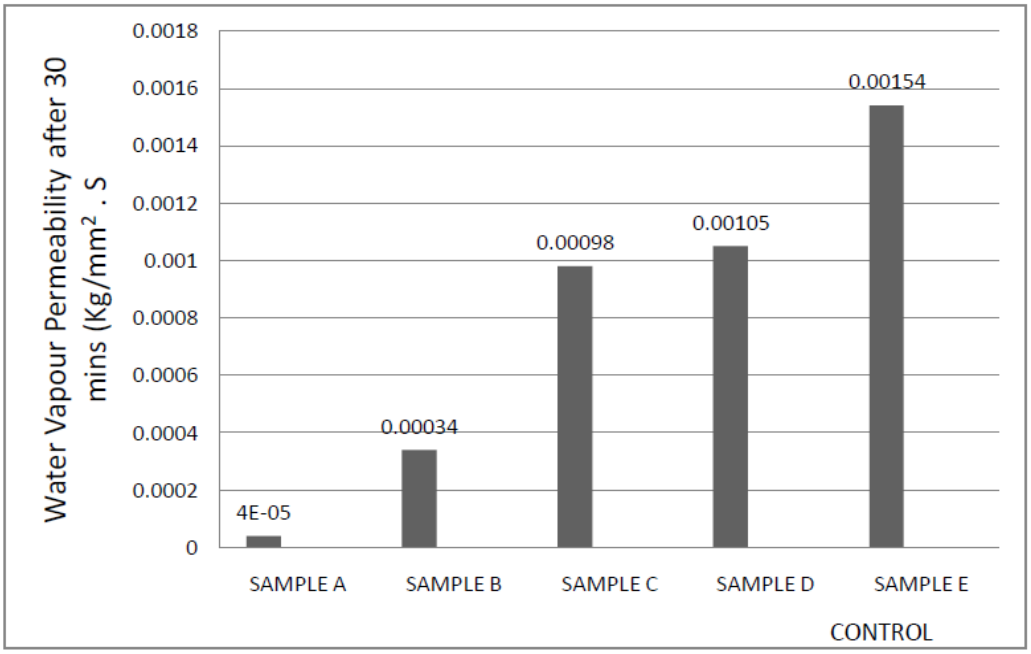

Fig 2. *Water Vapour Permeability of the Produced Film after 30 mins*

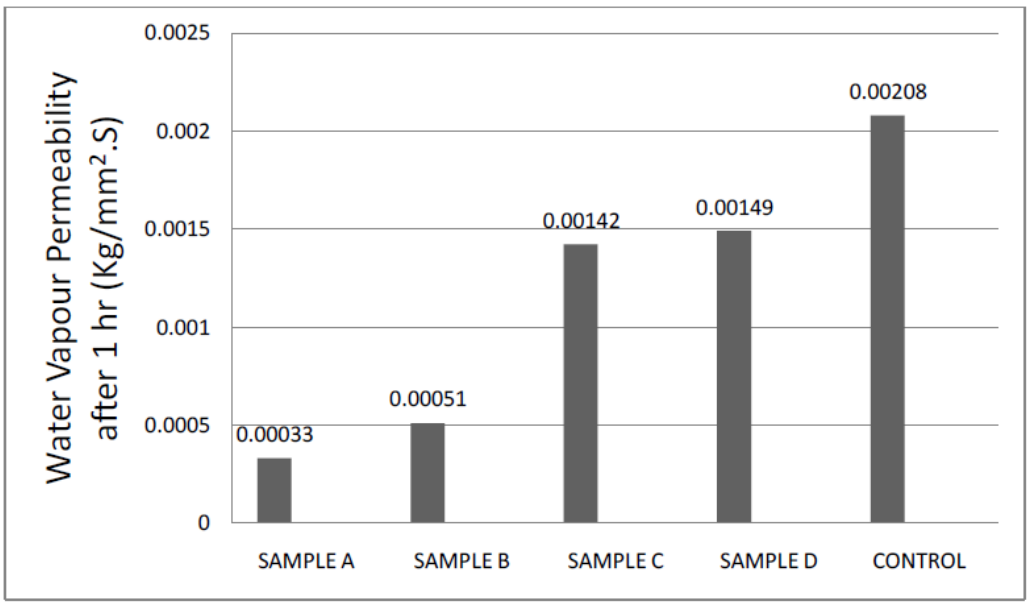

Fig 3. *Water Vapour Permeability of the Produced Films after 1 Hr.*

CONCLUSION

In conclusion, a polymeric film blend of collagen hydrolysate extracted from chromed leather wastes, and starch isolated from mango seed embryo has been developed and characterized. The collagen hydrolysate has been shown to increase the shore A hardness of the produced starch-based films.

The water vapour permeability of the produced films has been improved by the presence of collagen hydrolysate. The addition of 0.45 g of glycerol into the film compositions enhanced

the hardness and the water vapour permeability of the samples; however, the films produced for all sample composition are extremely brittle.

With suitable modification, polymeric films made of collagen hydrolysate and starch can be suitable for applications in agricultural mulches, packaging and wrapping because of their excellent biodegradability, good film-forming ability and similar mechanical properties to that of the synthetic films.

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