Morphological Lattice Micrograph Properties of Cow Bones Collagenous Unmodified and Hydrophobically Modified Gelatin Film

MUHAMMAD DAHIRU FARURUWA*, SYLVESTER SIMON AGABA, FELIX J O SYLVESTER
DEPARTMENT OF CHEMISTRY (MATERIALS SCIENCE AND EXPLOSIVE)
NIGERIA DEFENCE ACADEMY (NDA) KADUNA
NIGERIA

Abstract: Collagen is the main connective protein in the body of an animal predominantly found in the bones and skin of mammals. It is the primary source for gelatin recovery when subjected to a denaturing process at a control temperature. The aim of this study is to extract gelatin by hydrolysis, modified and determining by gravimetrical and scan electron micrograph characteristics of both the unmodified and fatty acid ester modified gelatin; the gelatin extraction percentage yield on a dry basis from collagenous cow bone after 20 hrs hydrolysis is 23.2%. The modified gelatine film subjected to hydrophocity test shows that water vapour transmission capacity of 3.9 x 10-8 gmm-1pa-1hr-1 was experimentally obtained by gravimetry desiccant method which implied that the hydrophobicity of the modified gelatine film is high to a stable accuracy. Comparison of microstructural and morphological properties of unmodified and hydrophobically modified gelatine films shows that a face cubic center (FCC) plane grain boundaries with a fibre internal structure of 1.29µm, 2.4 µm and 7.88 µm and pore average height, thickness area of 0.41µm², 1.44 µm² and 103.10 µm² respectively at a stable frequency were noticed in the unmodified gelatine and this explaine it brittle and surface wettability behavior. The hydrophobically modified gelatine has a rough surface region of a micro-structural morphology of a body cubic center (BCC) micrograph with a semi-crystalline lattice structure due to the present of a rod-like curve amorphous solid and a tetrahedron ice crystal solid on a rough surface region with fibre internal structure of 757.07 nm, 4.18µm, and 14.01µm and pores of average dept, thickness and area of 0.41 µm², 2.32 µm² and 22.98 µm². Roughness of the surface region confirmed it hydrophobicity ability. The modified gelatin obtained from collagenous cow bones formulated an environmentally friendly bioplastizer or binder for explosive synthesis.

Keyword: Bones, Collagen, Extraction, Gelatin, Hydrolysis, hydophobicity, Permeability, Semi-crystalline, wettability, FCC, BCC

1.0 INTRODUCTION

In order for an adhesive to bond (hold together) two surfaces (substrates), there must be several types of interaction between the adhesive and both substrates. The first type of interaction is that the adhesive must wet the substrate, meaning that the adhesive must spread itself out into a film that covers the substrate surface. In order for this to happen, the adhesive must have a low enough viscosity so that it will flow. Viscosity is the resistance of a liquid to flow. Because viscosity is temperature dependent, the application of a cold adhesive to a substrate, or the application of an adhesive to a cold substrate, may result in poor wetting. Another factor that affects wetting is the relative strengths of cohesive forces (between like molecules, such as two adhesive molecules) and those of adhesive forces (between unlike molecules, such as an adhesive molecule and a substrate molecule). If the cohesive forces among adhesive molecules are weaker than the adhesive forces between the adhesive molecules and the substrate surface, then the adhesive molecules will spread out over the substrate and wet its surface. An adhesive that has a relatively low viscosity and is able to wet the
substrate surface will flow into any tiny cracks or pores on the substrate surface, thus promoting what is known as mechanical bonding. Mechanical bonding increases the strength of an adhesive bond and, as a result, a forced separation of the two substrate surfaces is more apt to tear the substrate surfaces, [3].

Adhesives have been used for thousands of years, but until 100 years ago, the vast majority was from natural products such as bones, skins, fish, milk, and plants. Since about 1900, adhesives based on synthetic polymers have been introduced, and today, there are many industrial uses of adhesives and sealants. It is difficult to imagine a product – in the home, in industry, in transportation, or anywhere else for that matter – that does not use adhesives or sealants in some manner. Both adhesives and sealants work by adhesion phenomena. Adhesion is the attraction between two substances resulting from intermolecular forces that is establish between them. This concept is different from that of cohesion which only involves intermolecular forces inside one substance. The intermolecular forces that exist in adhesion and cohesion are mainly van der Waals type forces. Mechanical, electrical, and diffusion phenomena may also occur at the adhesion level [17].

Adhesives can be classified in to two broad part based on the origin of their primary components. They include natural and synthetic adhesives. Which are further divided into several groups

Synthetic adhesives are manufactured from industrial raw materials that have no natural origin. They include resins mainly based on urea, melamine, phenols, resorcinol, furan, epoxy and other unsaturated polyesters. Other resins are based on cellulose esters, ethers, alkyd and acryl esters, and polyamide, polystyrene, polyvinyl alcohols and their derivatives [11]

Natural adhesives are those whose primary components are either plant or animal based. Plant-based sources of adhesives include starches, dextrins, natural rubber and vegetables such as soya beans and peanuts. Animal-based sources of adhesives include hide, sinews, bones, hoofs, horns, fish skin and casein from milk curd. Animal-based adhesives were common in the history of woodwork. [11].

As it was mentioned earlier, the term natural adhesives refers to substances that are formulated from substantially or totally bio-based raw materials, which are used as adhesives in man-made technology.

Adhesives based on natural formulations have certain advantages: easily available, stable quality, non-toxic and biodegradable, environmentally friendly, and relatively low cost. Natural adhesives are both from organic (starch, casein, blood, animal hide and bones etc.) or inorganic (soluble silicates, cements, etc.) origin. [20] [9].

1.1 ANIMAL ADHESIVE (GELATIN)
Collagen is the main connective protein in animals, and hence is used as the basic component of most animal glues. There are two main sources of collagen: hide and bone from cattle. It is hydrophilic in nature. The collagen-based adhesives are obtained by denaturing the high molecular weight proteins through an acid or basic hydrolysis at moderate temperature. For higher strength collagen adhesives, intramolecular cross-linking is achieved by oxidative removal of amine groups of certain amino acids in the proteins, to form aldehydes.

Animal glues have limited resistance to water, mold growth, and vermin attack. Dry granulated products are prepared in warm water solution, and extended to form a tacky viscous film that on cooling gels to provide an intermediate, moderately strong bond. Heating the adhesive above 60°C should be avoided because of degradation. In order to optimize their properties for specific applications, certain additives are common in the commercial formulations: wetting agents, dispersing agents, gel depressants, chemical reactants, and plasticizers. It is also possible to use these adhesives in combination with other natural products, such as starches and dextrins.

Animal glues are derived by the hydrolysis of the protein constituent collagen of animal bones and hides. Collagen molecules are triple helices of amino acid sequences and contain both non-polar and charged acidic and basic side chains. The conversion of collagen to the soluble protein of animal glue (gelatin) involves breaking the intra and intermolecular polypeptide bond through the use of acid or alkali and heat. The collagen – glue (gelatin) transition has been described as a step-wise process involving the melting of the triple helix network to an amorphous form, followed by the sequential hydrolysis of various types of covalent bond, [24].

Animal glue (gelatin) is described as hydrolyzed collagen as shown in equation 1

$$ C_{102}H_{149}O_{36}N_{31} + H_2O \rightarrow C_{102}H_{151}O_{36}N_{31} $$

Collagen Animal glue

Animal glue (gelatin) is composed of α-amino acid joined in polypeptide linkage to form long chain polymers, (Eastoe and Eastoe1958). The typical chain fraction with three amino acids is shown in Figure 1.1
In aqueous solution of animal glue (gelatin), the polypeptide chain takes up random configurations of essential linear form. Studies have indicated that most glue molecules consist of a single chain terminated at one end by an amino acid and at the other end by a carboxylic group [27]. The molecule may also have side chain and contain cyclic structures. They may in part conform to the oriented chain in collagen [14]. Two methods have been adopted for the production of adhesive (glue) from bones. One consists of exposing bones to moist pressure (steam pressure) at temperatures above 100°C whereby the collagen (glue yielding substance) contained in the bones is transformed in such a manner that it is soluble in hot water. This method may be indicated briefly as the pressure method. The other method consists of completely extracting all the inorganic constituents, the phosphate of lime from the bones by the action of acids, where upon the remaining bone cartilage, the collagen, can be caused to change into glue without pressure by means of hot water. This method may be referred to as the maceration method. The maceration method yields a better bone adhesive due to its ability to maintain a control temperature of denaturing.

It was reported by (Nimni and Harkness 1988) that collagen is a multifunctional family of protein of unique fibrous structural characteristic and it is the most abundant protein in the body of mammals and function in good capacity ranging from serving crucial bio-mechanical function in bones, hide, tendon and ligament to controlling cellular gene expressions.

According to (Shu-Tung, 2000) collagen molecule like all protein are formed in-vivo by enzyme regulated step-wise polymerization reaction between amino and carboxyl group of amino acids where R represent a side group of amino acid residue as shown in Figure 2.1

![Simple structure of amino acid with a side group of amino acid residue R](image)

Fig: 2.1: simple structure of amino acid with a side group of amino acid residue R

Glycine (R=H) is the simplest amino acid with a hypothetical flat sheet organization of polyglycine molecules formation which is stabilized by intermolecular hydrogen bonding (Fig 2.1.1 a). However when the R-group is large as in most other amino acids, the stereochemical constraint frequently force the polypeptide chain to adopt a less constraining conformation by rotating the bulky (large) R group away from the crowded interactions forming a helix. (Fig. 2.1.1b). The hydrogen bonds are allowed to form within a helix (triple or α-helix) between the hydrogen attached to nitrogen in one amino acid residue and oxygen attached to the second amino acid residue.

![Hypothetical flat sheet structure of protein](image)

Fig. 2.1.1 (a) hypothetical flat sheet structure of protein (b) Helical arrangement of protein chain

(Branson et.al, 1951) determine that collagen exist as a molecule that is tightly coiled about itself forming a secondary structure termed as α-helix and when extracted from hides, tendon and bones becomes the primary component forming animal adhesive (glue). They are formed from long thin fibres of amino acid covalently bonded in a specific sequence [26].

### 1.2 Composition of Amino Acid in Collagen and Animal Glue

Amino acid studies corroborated by various analyses from scholars indicated that there are eighteen (18) different compositions of amino acids present in collagen and animal glue in varying amounts (Table 2.1). The acidic and basic functional groups of the amino acid and terminal groups confer polyelectrolyte characteristic to protein chains. The chains contain both amines and carboxylic group which are reactive and ionizable. These electrically charged sites affect the interaction among protein molecules and between protein molecules and water. The polar and ionizable groups are believed to be responsible for the gelation and characteristics properties of animal adhesive [30].

The development of biodegradable polymer in biomedical and bio-polymer application has attracted the interest and attention of many great scientists.
Animal adhesive (gelatine) has much adhesive binding effect which makes it an extensive source for bioactivity of non toxic biodegradable hydrophilic compactable materials. Animal adhesive have been broadly applied in various chemical, biological and medical field, such as its wide range application in the woodwork, pulp and paper, matches, pharmaceutical and textile industries.[4]

Animal adhesive (gelatine) even though it contains many glycine, proline and hydroxyproline residues, the solubility of the adhesive in water and the poor mechanical strength limit it utilization as a result prevent its hydrophobic functional ability for use as bio-plastic plasticizer for military explosivehowever, in a research work reported by Miyuki (2012), indicate the possibility that hydrophilic animal adhesive can be hydrophobically modified by modifying the primary amino group with various hydrophobic groups such as saturated hexanoyl, palmitoyl and stearoyl groups and unsaturated oleoyl groups through the nucleophillic substitution of the fatty acid ester with the primary amine [10].

Anhdrides, aziridines, expoxydes, aldhydes and hexons have been used for animal adhesive (gelatin) modification, (Clark et.al. 1977) with formaldehyde being one of the most frequently used reagent in gelatin network for non-food uses.

Charulatha (2003) observed that the chemical treatment of collagen caused an increase in thermal stability and tensile strength. In view of the literature carvalho et.al (2005) subjected their study objective on the evaluation of the effect of changes in the polymeric matrix through the addition of reticulant agents on solubility in water. The following properties water vapour permeability, colour parameter tensile strength and morphology of the gelatin based modified films were determined in comparism with the unmodified gelatin.

The parameter properties determination for water vapour permeability (WVP), Tensile strength (TS), and its Elongation (%E), colour luminosity (L) and parameter opacity where carried out.

### 2.0 METHOD OF EXTRACTION

2.0 kg of fresh Cow bones was crushed to 5 diameter particulate size in a crushing machine and washed thoroughly to remove stone particles and blood marrow trace from the flakes, there after dried for 48 hour. 500g of the bones were measured and macerated for 1.0 hour with 500 cm³ of 0.5M H₂SO₄ acid to remove some fraction of lime phosphate from the bone.

The pretreated bone flake was then hydrolyzed at a control temperature of 60° C with hot water in an extraction pressure pot for 20 hr until a large part of the gelatin adhesive contained in the bone completely hydrolyzed in water. The extracted bone adhesive was filter into 500cm³ beaker with soil screen sieve of nominal mesh size ranging from 60mm to 20µm diameter, then centrifuged for 20 minute at revolutionary rate of 60 rpm and afterward decanted to remove all the greases suspended particles. Finally the gelatin gel concentrate was ovum dried for 24 hr at control temperature of 37 °C to remove the remaining water content. The gelatin gels solidify into cake on cooling after removal from the ovum dryer [8].

### 2.1 METHOD OF MODIFICATION

To modify the gelatin (Animal bone adhesive) 8.0g of gelatin was weigh and added to the solution of 50cm³ dehydrated dimethylsulfoxide (DMSO). 0.6 cm³ of triethylamine (TEA) was also measured and add to the mixture above. The mixture was thoroughly stirred at 35 °C, for 30 minute in a water bath until the gelatin completely dissolved. 50% of the gelatin amino group was substituted with a hydrophobic unit fatty acid ester by adding 1 cm³, 2cm³, and 3cm³ of palmitoyl (fatty acid ester) to the gelatin solution above. The mixture was stirred thoroughly to obtain homogeneity. 20 cm³ of ethanol was added to the mixture three times, a White precipitate solution with cloudy lump precipitate formed. The cloudy lump precipitated hydrophobic modified gelatin was rinse thoroughly with 80cm³ ethanol in a 250 cm³ beaker until a milky like hydrophobically modified gelatin plasticizer (HMG) emerge [10]. The HMG Plasticizer was dried and subject to gravimetric analysis using desiccant method by weighing its weight and place in a desiccators to determine its water vapor permeability level [2].
2.2 METHODS OF ANALYSIS
Gravimetrical Method of Analysis on the Hydrophobic Modified Gelatin

Water vapour permeability test
4.2g of hydrophobically modified gelatin HMG Film sample was filled with silica gel and incubated at 25 °C for a relative humidity gradient of 50%. The film cell was weigh at 6.00 hr interval daily for a period of 14 days until a constant weight is achieved and water vapour permeability test was determine gravimetrically using the equation

\[ WVP = \frac{w}{t} \times \frac{x}{A P_o (R_{H1} - R_{H2})} \]

Where w/t is the change in mass (flux, g/h) x is the film thickness (mm), A is the area of the film surface exposed to permeant (m²), P_o is the vapour pressure of pure water (kpa) and (RH₁ - RH₂) is the relative humidity gradient used in the experiment at 25°C (P_o is 3.159 kpa) [10].

Scan Electron Microscopy SEM Morphology of Modified and Unmodified Gelatin Film Analysis

Scan electron microscopic machine was used to analyse the micro-structural morphology of the modified and unmodified gelatine film in accordance to a lay down SEM procedure by [6].

Unmodified and modified gelatine film was cut to 5mm² area and mounted on a stubs and sputtered coater with an ultra thin layer of gold Au for 1 minute at 5mm so as to make it electrically conductive. The both gelatine film surface cross-section were study with Pro X phenom world scanning electron microscopic machine operating at 15kv for 500x magnification images. The unmodified and modified gelatine film fibre bundles diameter and pores areas where measured from the SEM and a micrographic images of the gelatine film cross-section captured respectively [6].
3.0 RESULT AND DISCUSSION

3.1 GELATIN EXTRACTION YIELD (%)
The Gelatin extraction percentage yield was calculated on a dry basis to be 23.2% yield for the dry weight of 116g gelatin extracted from 500g collagenous bone material subject to hydrolysis process after 20hr. the formular used to determine the percentage yield is expressed thus [31].

\[
\text{Yield} \, (\%) = \frac{\text{Dry weight of Extracted Gelatin}}{\text{Dry weight of bone raw material}} \times 100
\]

3.2 Gravimetric Determination of Water Vapour Permeability Test on Hydrophically Modified Gelatin HMG Plasticizer

Water vapour transmission test was conducted on the modified gelatine film with a rectangular surface area of 374.9 mm² and thickness of 10.00 mm to determine its hydrophobicity level using the desiccant method under a relative humidity of 50% at an ambient temperature of 25°C as described by ASTM 96 (1995). The gravimetric test by desiccant method shows a continual decrement in water mass through evaporation on the modified film. Table 3.5 shows that during the experiment there was a continual weight loss of the modified gelatine until a constant weight decrement took place at 288 hr from the initiation. From the result of weight loss of modified gelatine over elapse time experiment as shown in table 3.5 a plot of weight against elapsed time of the entire experimental duration was carry out and a negative curve line which tends to be straight emerge as display in fig 3.5.1. The straight line plot on the graph tends to fit into four proper space point which indicate that the periodic change in weight marches and a steady state is slightly assume [23]. The regression 0.768 deduce from the plot point in the graph Shows that the level of the hydrophocity or water transmission as the modified gelatine tends to be constant is nearness to unity, this imply that the periodic change in weight of modified gelatine tends to be slightly stable.

<table>
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<th>Weight of petridish: 7.46g</th>
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<tr>
<td>Length of rectangular shape HMG film: 23.00mm</td>
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<tr>
<td>Breadth of rectangular shape HMG film: 16.50mm</td>
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<td>Area of HMG film: 374.9 mm²</td>
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<td>Relative humidity gradient: 50%</td>
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<td>Time interval duration: 24 hours daily</td>
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<td>Partial vapour pressure of pure water @ 25°C: 3.159 kPa</td>
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<th>6.00 hr interval</th>
<th>Weight (g)</th>
<th>Weight (g)</th>
<th>Wav (g)</th>
<th>Thickness (mm)</th>
<th>Time (hr)</th>
<th>Wavt (g/hr)</th>
<th>WVP (RH1-RH2) (g kPa⁻¹ mm⁻¹ hr⁻¹)</th>
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The water vapour permeability of the modified gelatine was calculated using the relationship

\[
\text{WVP} = \frac{\Delta w_{av}}{\Delta t} \times \frac{x}{A P(b(RH1-RH2))}
\]
The rate of transmission ($\Delta w/\Delta t$) which equally represent the slope was calculated to be 0.00213 mhr$^{-1}$, the calculated result shows that the water vapour transmission level of the modified gelatine is 3.9 x 10$^{-5}$ (gkpa$^{-1}$mm$^{-1}$hr$^{-1}$). From the calculated water vapour permeability it can be concluded that the hydrophobicity of the modified gelatine film is high to an accuracy precision of 3.9 x 10$^{-8}$ gmm$^{-1}$pa$^{-1}$hr$^{-1}$. Which indicate that the modified gelatine film is hydrophobic?

3.3 COMPARISON OF MICROSTRUCTURAL AND MORPHOLOGICAL PROPERTIES OF UNMODIFIED AND HYDROPHOBICALLY MODIFIED GELATINE FILMS

Micro structural morphology of the unmodified gelatine film extract and the hydrophobically modified gelatine film was study using scan electron microscopy (SEM). The elemental analysis of the both gelatine film was investigated using bar scatter detector full (BSD full) on a maximum of 500x magnification of 15kv imaging capacity.

The result review that the micro -structural morphology of the unmodified gelatine film show s a face centre cubic (FCC) plane grain boundaries with a fibre internal structure ranging from 1.29µm, 2.4 µm and 7.88 µm and pore average height, thickness and area of 0.41µm$^2$, 1.44 µm$^2$ and 103.10 µm$^2$ respectively at a stable frequency as shown in the fibre and pore histogram in fig 3.8 (c) (e)

The unmodified gelatine film was discovered to have a compact orientation separated by a straight line crack and an interface bonding containing circular dot. The straight line crack and circular dot intermolecular bonding indicate the cross linking bonding interaction of the unmodified gelatine network in its micro-graphical state and as a result increases the brittleness and when subject to failure test analysis can easily fracture or break due to its level of brittleness [6].

wettability occur when a the lattice micro-structural surface morphology tends to be smooth [7]. The effect of the plane grain boundary region of the surface microscopic opening and the straight line crack formation in fig 3.8 (a) shows that the unmodified gelatine film exhibit high surface wettability. The crack was also observed to have emerged during drying and rupture as a result of the evaporation induced pressure. The crack initiation and propagation explain why the unmodified gelatine has high wetting nature and more hydrophilic due to its large pore area [7].

The result of the hydrophobically modified gelatine in fig 3.8 (b) shows a rough surface region of a micro-structural morphology containing body centre cubic BCC on the modified gelatine film with fibre internal structure ranging from 757.07 nm, 4.18µm, and 14.01µm and pores of average dept, thickness and area of 0.41 µm$^2$, 2.32 µm$^2$ and 22.98 µm$^2$ respectively as shown in the modified fibre and pores histogram in figure 3.8.1 (d) (f)

The modified gelatine film was discover to have a body centre cubic BCC micrograph of a semi-crystalline lattice...
structure due to the present of a rod-like curve amorphous solid and an tetrahedron ice crystal solid. The semi-crystalline lattice structures formed on the rough surface region of the modified gelatine film shows that the modified gelatine film exhibit direct behaviour of a polymer because of the present of the amorphous solid and ice crystal lattice structure on the rough micrograph of the modified gelatine. The crystal structure formed shows that there is a molecular lattice structure arrangement in a repeated pattern on the modified gelatine and as such have a compact orientation while the amorphous rod-like structure in the rough micrograph interpret that, the molecule of the modified gelatine film is arranged randomly and in long chain which twist and curve on each other. These make the orientation of the modified gelatine film unlikely. This behaviour of the semi-crystalline structures formed explains the plasticizer effect of the modified gelatine film. [15].

considering the wettability research work done by Ghosh et al, 2015, which highlight that the hydrophocity of a material increase with increase in the material surface roughness. It is therefore certified that the rough surface shown in figure 3.8 (b) indicate that the modified gelatin has a very low wettability capacity compare to the unmodified due to it surface roughness and small pores area and as such exhibit high hydrophobicity [7]
CONCLUSION

These research work formulated an expendable environmental friendly hydrophobic modified plasticizer (binders) which will serve a strong military application cutting across its used as military gadget adhesive to its use as explosive binders

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