International Journal of Engineering Research and Technology. ISSN 0974-3154, Volume 13, Number 12 (2020), pp. 4297-4304

Bioplastics Properties of Fish Scales and Their Effects on the Mechanical Properties in Biocomposites: A Review

D. O. BICHANG'A*, L. M. MASU & P. K. NZIU

Department of Mechanical Engineering, Vaal University of Technology, Vanderbijlpark, South Africa.

ORCID: 0000-0002-8544-6321(Prof LM Masu), 0000-0002-5899-0700 (PK Nziu)

Abstract

Fish scales obtained from most abundant aquatic species is regarded as waste of no or minimal economic value. However, recently, fish scales have been gainfully converted into value added bio-products such as bioplastics and bio-composites. The properties of fish scale bioplastics are greatly influenced by environmental conditions such as temperatures which influence imino acids composition. Several studies have concluded that the content of hydroxyproline imino acid content is dependent on the environmental temperatures in which the fish lives. Fish scales in both filler and powder form have been used as biodegradable reinforcement for composites fabrication. The effects of fish scale fillers or powder incorporation on the mechanical properties of resultant composites are divergent with some reporting decline while others increase in mechanical properties. This can be attributed to differences in fish species and testing methods used by various researchers. Therefore, this paper reviews bioplastics properties of fish scales and their effects on the mechanical properties in biocomposites.

Keyword: Fish scales, bioplastics, mechanical properties & bio-composites

1. INTRODUCTION

Bioplastic also known as biodegradable films can be obtained from different natural polymers like polysaccharides, proteins, lipids or their combinations [1]. The main advantages of natural plant proteins include low cost and readily available. Besides plant proteins, animal proteins from cow and fish [2] have shown excellent capacity to form bioplastics. Of all animal proteins, fish proteins have more advantages for bioplastic preparation. Some of these properties include ability to form networks, elasticity, plasticity and ability to serve as excellent oxygen barrier [3].

Fish protein exists in three groups, myofibrillar proteins [also known as structural proteins], sarcoplasmic proteins and stroma proteins [4]. Myofibrillar protein (MP) refers to structural protein that makes up 65-75% [w/w] of the total proteins in fish. These proteins are made of myosin and actin which play a significant role on functional properties such as water holding and emulsifying capacities, gelation and binding ability. Similarly, a study by [3] concluded that myofibrillar proteins account for emulsification, water retention and gelling properties of fish protein. On the other hand, sarcoplasmic protein constitutes of about 15-35% (w/w) of the total fish protein while the content of stroma protein ranges between 10-30% (w/w) of the total fish protein depending on fish species [4]. Some properties of sarcoplasmic protein include low water retention ability, low viscosity, low capacity to absorb colors and flavors, and high elasticity [3]. A research on effect of the ratio of myofibrillar protein and sarcoplasmic protein on properties of protein based film reported that the tensile strength of the film reduced with increase in sarcoplasmic protein content in the film. However, the water vapor permeability (WVP) of the film increased with increase in sarcoplasmic protein in the film [5]. The study, therefore, concluded that sarcoplasmic protein has high ability to adhere to myofibrillar protein thus preventing gel formation. The purpose of this paper is to review bioplastics properties of fish scales and their effects on the mechanical properties of resultant biocomposites. Therefore, the review of bioplastics properties of fish scales and their effects on the mechanical properties of the biocomposites are presented in this work.

2. BIOPLASTICS PROPERTIES OF FISH SCALES

Several studies on characterization of the functional properties fish protein-based bioplastics have been carried out. A study on characterization of chitin extracted from scales of marine fish species concluded that molecular structure of chitin is a high molecular weight polymer. Further, the study observed that chitin has a linear polyamine structure whose amino acids are readily available for chemical reactions [6]. A research to produce and characterize bioplastics prepared from myofibrillar protein found in *gilded catfish* waste reported that myofibrillar protein-based bioplastic had 96.58% protein, 2.86% ash content, 0.74% lipids and 0.06% moisture content [7]. Similarly, a study by [8] reported 86.9% protein, 2.33% ash content and 10.5% moisture content for lizardfish scale gelatin. Gelatin is a natural biopolymer obtained by thermal degradation of collagen [9].

Further review literature on fish scale bioplastics has shown higher protein concentrations. A research by [10] reported 78.2% protein, 0.10% ash content and 22.16% moisture content for tilapia scale bioplastics. Also, a study by [11] reported 64.74% protein, 1.80% ash content, 6.55% moisture content and 8.85% lipids. A research by [12] reported 89.7% and 88.6% protein content for freeze-dried gelatin extracted from bigeye snapper and brown eye snapper, respectively. In

International Journal of Engineering Research and Technology. ISSN 0974-3154, Volume 13, Number 12 (2020), pp. 4297-4304

addition, a study by [13] showed higher protein content of 90.4% and 89.8% for rohu and common carp biopolymer, respectively. On the other hand, the study reported lower ash, lipid or fat and moisture content. For biopolymer extracted from rohu fish species, the study reported 8.10% moisture content, 0.57% lipid and 1.18% ash content. Similarly, common carp reported 8.48%, 0.62% and 1.11% for moisture, lipid and ash content, respectively. According to the study, the lower fat and moisture content is an indication of higher efficiency of fat and water removal from the fish skin prior to biopolymer extraction.

From these studies, it is evident that fish protein-based bioplastics have high protein content and low ash content. A study by [7] explained that the high protein content is significant for the formation of biopolymer matrix. Similarly, a research by [14] concluded that the maximum possible yield of gelatin expected from collagenous materials is exclusively dependent on the protein content of the collagenous materials. Also, a study by [10] argued that the high protein concentration is a confirmation that protein can be obtained from fish scales. In addition, the concentration is based on fish scale microstructure reported in literature [15,16]. This implies that the higher the protein content, the higher the gelatin or biopolymer yield. On the other hand, low ash content has been reported for extracted fish protein-based bioplastics. For instance, gilded catfish bioplastic had 2.86% while lizardfish scale gelatin had 2.33% ash content. Although the recommended ash content for fish protein-based bioplastics is 2.6%. The lower the ash content, the higher the quality of extracted bioplastics.

A study to extract and determine the physiochemical characteristics of rohu and Common carp fish gelatin by [13] showed that the gelatins had high imino acid content of 20.5 and 19.2%, respectively. Further review literature shows no significant variations in imino acid content. For instance, the imino acid content for grass carp gelatin is 19.5% [17] and 19.9% for carp fish scale gelatin [18]. Similarly, a research by [12] observed no significant difference in imino acid content for both bigeye snapper and brown red snapper skin gelatins. The study reported higher imino acid levels of 22.5% for fish species. Generally, the amino acid composition was analogous to that of mother collagen reported by [19].

Proline and hydroxyproline significantly influence the gel strength of bioplastics [8]. Similarly, a study y [20,21] concluded that the content of imino acid, that is, proline and hydroxyproline significantly affects the functional properties of gelatin extracted from collagen. Further, the study explained that the lower the imino acid content of fish collagen, the lower the gel strength of fish gelatins. For instance, the gel strengths of lizardfish scale gelatin and bovine gelatin are 268 g and 322 g, respectively [8]. These variations in gel strength can be attributed to differences in imino acid content. Lizardfish scale gelatin has imino acid content of 20.4 % [8] while the imino acid content in bovine gelatin is 23.3% [17]. Therefore, the gel strength of bovine gelatin is higher than lizardfish scale gelatin.

A study by [22] extracted and characterized collagen from fish waste materials: skin, scales and fins of *C. catla* and *C. mrigala* fish species. The study observed that there was no significant difference in imino acid content for collagen extracted from skin, scales and fins for the two fish species under investigation. According to the study, the content of imino acid for *C. catla* fish and *C. mrigala* biopolymer was 16.3% and 16.4% for skin, 15.7% for scales of both species and 16.7% and 15.4% for fins, respectively. In addition, studies have reported imino acid content of 18.6% [23], 16.3% [24]. On the other hand, a research by [25] observed insignificant difference in imino acid content for scale collagens extracted from three different fish species. According to the study imino content levels were 19.7%, 19.6% and 19.3% for sadine, red seam bream and Japanese sea brass scale collagens, respectively.

Further review literature shows a higher imino acid content of between 19-22.1% for different fish species. A study by [26] observed imino acid content of 20.0% and 20.5% for acid-solubilized skin collagens of black drum and sheepshead, respectively. Whereas, similar work by [19] observed 21.2% and 22.1% imino acid content for Acid- and Pepsin-solubilized collagen brown stripe red snapper gelatins, respectively. Similarly, [27] reported 19.3% and 16.3% imino acid content for skin and bone bigeye snapper collagens, respectively. This finding is analogous to those observed by [23] who observed 19.3% imino acid content bigeye snapper skin collagen. Table 1 hereunder provides imino acid content (%) for some fish scale bioplastics presented in this review paper.

Table 1: Imino acid content (%) for some fish scale bioplastics

Fish species	**Imino acid %**	**References**
Carp	19.5	[18]
Lizardfish	20.4	[8]
C. Catla	15.7	[22]
C. Mrigala		
Sadine	19.7	[25]
Red seam bream	19.6	
Japanese sea brass	19.3	
Rohu	20.5	[13]
Common carp	19.2	
Brown red snapper	22.5	[12]
Begeye snapper		

2.1 EFFECT OF ENVIRONMENTAL TEMPERATURE ON BIOPLASTIC PROPERTIES

Studies by [19,27] have concluded that the content of imino acid [proline and hydroxyproline] of fish species vary with conditions in their living habitat. This conclusion is analogous to previous study [28] which concluded that the content of hydroxyproline imino acid content is dependent on the environmental temperatures in which the fish lives. This means that collagens extracted from fish species living in warm environments have higher contents of hydroxyproline than collagen extracted from fish living in cold environments. For instance, gelatin extracted from tilapia which is a warm water species contains higher imino acid content of 25.4% [29]. Further study by [25] observed that imino acid content is correlated with the temperatures of the water where the fish lives. A research by [30] on gelatins from cod skin observed lower imino acid for cod gelatin [cold water fish] compared to tilapia gelatin [warm water fish]. Also, a comparative study on skin gelatins from five different fish species by [21] observed lowest imino acid content in cod fish [15.6%] compared to 17.3-17.5% reported for other fish species in the study. The differences in environmental temperatures explain the higher imino acid levels of 30% reported for mammalian gelatins [31].

Solubility of extracted biopolymer is an important functional property in the conversion of collagen, which is insoluble in water, to water soluble gelatin (biopolymer). A research by [32] on silver catfish gelatin observed that the solubility of gelatin increased with extraction time. The study attributed this observation to prolonged hot water exposure during gelatin extraction process. Also, studies by [33,34] observed that the use of hot water in gelatin extraction breaks down complex triple helical structure into smaller gelatin molecules soluble in water. A study by [14] observed higher solubilities for young Nile perch skin collagen of 3.5% compared to adult skin collagen of 2.5%, indicating slight increase in extent of stable cross-links. Similarly, a previous study by [35] has reported increase in stable cross-links in collagen with age amongst mammals. This implies that the triple helical structure is more complex in adult fish hence lower solubility compared to young fish. A study by [7] on gilded catfish waste bioplastics reported 19.46% solubility. Similarly a research by [36] observed a solubility of 12.3-19.5% for Nile tilapia bioplastics. Bioplastic solubility is caused by loss of structural integrity of the bioplastic film and the degree of protein denaturation.

3. MECHANICAL PROPERTIES OF FISH SCALE BIOCOMPOSITES

Fish scale is an example of natural reinforcement for biocomposites fabrication with significant mechanical properties such as resistance to penetration, ultra-thin structures, compliance and light weight [37]. A study by [38] concluded that biodegradability of fish scale reinforced bio-composite increased with increasing content of fish scales in the composite. Similarly, a research by [39] concluded that addition of fish scale derived hydroxyapatite enhances the biocompatibility of the biofilms by improving their hydrophilicity. Besides, incorporation of hydroxyapatite particles improved the thermal stability of hydroxyapatite reinforced PLA polymeric biofilms. The proceeding subsections provide a review on the tensile properties, flexural properties and impact strength of fish scale reinforced biocomposites.

3.1 Tensile Properties of fish scale reinforced biocomposites

A study by [40] on bio-wastes hybrid composite prepared at 5% fish scale (FS) and 5% pine cone (PC) mono-filler and hybrid composites at 5, 10 and 15% with 50/50 FS/PC composition in the hybrid reported higher tensile strengths for composites with 5% mono-filler compared to hybrid composite. The 5 wt% FS mono filler composite reported tensile strength of 65.66 MPa while 5 wt% hybrid composite reported 60.09 MPa. The study further showed the tensile properties of hybrid composites reduced with increase in fish scale flakes loading. According to the study, the trend can be attributed to increase in the number of spaces or voids in the composites [40].

On the other hand, research by [41] reported increase in ultimate tensile strength and percentage elongation with increase in fish scale in hybrid composite up to 3 wt% due to superior bonding at the matrix/reinforcement bonding. However, the composite exhibited brittle characteristics as fish scale increased thus significantly reducing tensile strength and percentage elongation. Similarly, a study by [40] reported no significant improvement of the tensile properties of the composite with hybridization of fish scale with pine cone powder. However, research findings by [42,43] have concluded that hybridization significantly improves the mechanical properties of resultant composites.

Additionally, [44] studied the mechanical, structural, thermal and morphological properties of fish scale composites. The study varied the content of fish scales in the composites from 5 wt% to 20 wt%. The findings showed decrease in tensile strength and tensile modulus of the resultant composite with increase in fish scale content. The study attributed this trend to weak interfacial bond strength vulnerable to de-bonding under tensile loading leading to failure of the composite. Moreover, a study by [45] on mechanical properties of powdered catla fish scales reinforced propylene composite reported gradual decline in composite tensile strength with increasing fish scale content in the composite. Similarly, the total elongation of the composite reduced as the content of fish scale in the composite increased. The study attributed this trend to agglomeration of fish scale particles at higher content.

Further review literature by [46] concluded that addition of fish scale powder to wheat gluten based bioplastic increased the tensile strength of the resultant composite. According to the study, the tensile strength of fish scale powder reinforced composite was double the tensile strength of neat wheat gluten bioplastic. Hydroxyapatite-protein interaction and protein [wheat gluten]/protein [collagen] crosslink improved the tensile strength of fish scale powder reinforced composite. Further, scanning electron microscope (SEM) micrographs showed smooth surface for neat wheat gluten bioplastic. On the other hand, fish scale powder reinforced wheat gluten showed good dispersion of fish scale powder within the matrix, proving further evidence of enhanced tensile strength of fish scale powder reinforced composite. In contrast, a study by [38] concluded that incorporation of fish scale decreased the mechanical properties of fish scale reinforced propylene composite. Fractured specimens showed that the fish scales were not uniformly distributed in the matrix thus some areas of the composites lacked reinforcement. Hence, mechanical properties reduced with increase in the fish scale content in the composite.

In contrast, an experimental investigation of fish scale reinforced epoxy composites by [47] showed a mixed trend in tensile strength with increase in fish scale content. The study reported decrease in tensile strength as fish scale content increased from 10 to 20 vol%. This was attributed to the particulate form of fish scale reinforcement incapable of actively bearing the applied load. Similarly, a study by [48] attributed decrease in tensile strength with fish scale reinforcement to two main reasons. First, the chemical reaction at the fish scale/matrix interface was too weak to transfer the applied loads. Secondly, there was high stress concentration in the epoxy matrix due to irregular shape of fish scales. On the other hand, a study by [47] reported increase in tensile strength as fish scale volume increased from 20 to 30 vol% to attain maximum tensile strength at 30 vol% due to good interfacial adhesion [44]. Further, the tensile strength decreased as fish scale volume increased from 35 to 40 vol% as a result of agglomeration of fish scale filler in the epoxy matrix.

3.2 Flexural Properties of fish scale reinforced biocomposites

On flexural properties of fish scale reinforced composite, [44] reported an increase in flexural strength and flexural modulus with fish scale loading from 5 to 15 wt%. Similarly, a study by [49] on mechanical properties improvement by incorporating fish scale hydroxyapatite filler reported increase in flexural strength and modulus with hydroxyapatite loading up to 10%. The increment in flexural properties was attributed to chain mobility restriction resulting from inter- and intra-molecular interaction between epoxy matrix and protein structures of the fish scales. Incorporation of fish scale fillers into epoxy matrix significantly improved the flexibility of resultant composite compared to neat epoxy composites. This was caused by higher proportion of highly flexible protein structures that were introduced into polymer matrix. Further review literature by [50] concluded that incorporation of snail shell hydroxyapatite fillers significantly improved the mechanical properties and wear resistance of the composite. This was due to uniform dispersion of HAp fillers in epoxy matrix. The increase in flexural strength of the composite with incorporation of any mineral filler has been reported previously [51] where filler-matrix interaction makes the composite more stable against flexural forces. However, [44,49] reported decline of flexural properties as fish scale (FS) filler increase beyond 15% and 10%, respectively. The studies attributed the decline in flexural properties to particle agglomeration causing insufficient interfacial bonding between fish scale fillers and epoxy matrix. Therefore, as dispersion becomes poor, flexural strength and elastic modulus decrease. Further, [44] concluded that at filler loading beyond 15 wt%, the maximum fixed proportion of epoxy exceeded the FS-FS interaction causing decline in flexural modulus.

3.3 Impact Strength of fish scale reinforced biocomposites

A study by [45] on the mechanical properties of catla fish scale reinforced polypropylene (PP) composites concluded that the impact strength decreased with increasing fish scale reinforcement. Similarly, a research by [38] reported decrease in impact strength as waste fish content in the composite increased. This was attributed to poor interfacial adhesion between the matrix and reinforcement. Additionally, the particle size of the fish scale reinforcement in dispersed phase contributed to the decline of impact strength with increasing fish scale content in the composite. On the effect of fish scale incorporation in PP matrix, the study showed that neat PP composite exhibited higher impact strength compared with fish scale polypropylene reinforced composites.

Studies by [41,44,49] reported similar trend of increasing impact strength with increase in fish scale filler loading due to good matrix-filler adhesion in the composites. The increase in impact strength was attributed to excellent blending of fish scale reinforcement as well as enhanced adhesion between reinforcement and matrix. Also, fish scale reinforced epoxy composite exhibited higher impact strength compared to neat epoxy as incorporation of fish scale fillers improves the toughness of the resultant composites. Protein structure present in fish scales with capability to absorb impact energy can be attributed to higher impact energy of fish scale reinforced composites compared to neat epoxy. Fractured surface of neat epoxy indicated brittleness of epoxy resin. Further, the studies reported that increasing filler content leads to agglomeration thus reducing the impact strength of the resultant composite.

A study by [48] on erosion behavior of fish scale reinforced composites reported marginal improvement in hardness and reduction in tensile strength with incorporation of fish scale reinforcement. The study further showed that during tensile loading, the filler matrix interface is susceptible to debonding. Also, during hardness testing, the solid filler and matrix phases are pressed together hence touching each other tightly as a result of compression stress. These explain increase in hardness and decrease in tensile strength with incorporation of fish scale filler into the composite. Further studies by [40,45,52] have reported increase in hardness properties with increase in fish scale reinforcement in the composite. This has been attributed to improved adhesion between fish scale reinforcement and matrix interface resulting into reduced micro-voids and matrix-reinforcement de-bonding at the interface. Further, the studies concluded that incorporation of fish scales improves the impact properties of the composites as fish scale reinforced composites showed higher impact strengths than neat epoxy or polypropylene composites.

4. SUMMARY AND DISCUSSIONS

Proteins are made of amino acids. Fish protein-based bioplastics comprise of different amino acids of different proportions. A study to determine the optimal conditions for gelatin extraction from lizardfish scales concluded that the content of imino acid [proline and hydroxyproline] and glycine in lizardfish scale gelatin was 20.4% and 18.3%, respectively [8].

Similarly, a research by [14] reported higher total imino acid content of 20% and 19.3% for adult and young fish skin collagen, respectively for Nile perch skin. Therefore, according to the study there was no significant difference in imino acid between young and adult Nile perch skin gelatin. However, slightly higher imino acid content of 25.4% have been reported for tilapia fish [29] which is the highest reported imino acid content for fish collagens. Proline and hydroxyproline which constitute imino acid are related to gelling properties, that is, the lower the content of imino acid, the gelling power of bioplastics tends to be lower and poorer.

The levels of imino acid especially hydroxyproline affect the thermal stability and denaturation temperature of the extracted collagens. A research by [53] has observed higher denaturation temperatures of 32.4^0C, 35.8^0C, 37.8^0C and 32.0^0C for collagen extracted from fish skin, scale, bone and fin wastes, respectively. In another study, [54] reported denaturation temperature of $27\text{-}28^0$C, $31\text{-}32^0$C and $30\text{-}32^0$C for skin, bone and muscle collagen, respectively. A study by [55] on several fish bone collagens observed a denaturation temperature of 37.0^0C. However, a study by [56] reported lower denaturation temperature of 28.0^0C for carp fish skin, scale and bone acid-solubilized collagens. Hence, no significant difference in denaturation temperature values of acid-solubilized collagens extracted from different parts of the carp fish.

A study by [14] reported higher denaturation temperature of 36.0^0C and 36.5^0C for young and adult Nile perch fish collagen due to higher imino acid content compared to collagen obtained from cold environments. According to the study, the small difference between denaturation temperatures indicated minimal differences in the extent of stable cross-links. Further review literature has concluded that denaturation temperature of collagen extracted from fish species living in warm environments is higher than those from cold habitats [56]. Further studies by [57, 58] have concluded that fish species from cold environments have lower hydroxyproline [imino acid] content hence lower denaturation temperature compared with fish species from warm environments. This explains the highest denaturation temperatures reported for mammalian collagens as mammalian habitat is warmer than that of fish species.

Similarly, a research by [59] concluded that the thermal stability of collagen is dependent on imino acid content. Therefore, the collagens extracted from fish species living in cold environments exhibit lower thermal stability compared to collagen extracted from fish species living in warm water. This can be attributed to the fact that hydroxyproline takes part in hydrogen bonding thus stabilizing the triple helical structure of collagen [15,19]. Further, [60] observed that both proline and hydroxyproline have pyrrolidine ring. This ring serves to strengthen the triple helix of the collagen by enforcing restrictions on the conformation of polypeptide chain. Although fish species living in cold environments contain lower imino acid content, research has shown that these fish species have higher content of threonine, serine and hydroxyl amino acids. However, not much research has been carried out to study the effect of these acids on functional, physiochemical and rheological properties of gelatin extracted from fish species living in cold environments.

Although most studies have observed that fish protein-based biopolymer has higher imino acid content of 22.5% [12] than any other type of amino acids, other studies have reported divergent findings. A study by [19] on isolation and characterization of Brownstripe red snapper collagen observed that the collagen had highest glycine content of 25.2% compared to 21.2% imino [proline and hydroxyproline] acid content. Similarly, a research by [22] concluded that glycine was the most amino acid followed by alanine for all fish species investigated. Collagen from leather jacket fish trash has been reported to have the highest levels of glycine of 35.2-35.7% compared to 16.1%-19.0% imino acid content [54]. A study by [61] observed high levels of glycine, proline and hydroxyproline amino acids carp fish scale collagen. Further studies by [23,56,62] have also demonstrated that glycine constitute of higher proportions of all amino acids in each collagen type characterized. However, [63] reported the highest concentration of aspartic acid of 12.1% for Nile tilapia myofibrillar protein. This divergent trends observed in the reviewed studies can be attributed to differences in environmental conditions such as temperature of the living habitat of the species. Although, several studies have reported that some fish collagen contain higher glycine content, not much research has been conducted on the effect of glycine on physiochemical, functional and rheological properties of the resultant biopolymer.

A study by [52] on fabrication, mechanical characterization and FTIR spectroscopic analysis of fish scale reinforced epoxy composites reported a decline in tensile strength as fish scale content in the composite increased from 5 wt% to 15 wt%. Similarly, a research by [48] concluded that the tensile properties of the composite reduced with increase in fish scale reinforcement due to incomplete matrix fusion and poor interfacial adhesion. Poor interfacial bonding between the matrix and fish scale as well as incomplete matrix wetting were responsible for reduction in tensile-strength properties of the composites with increase in fish scale content. Nevertheless, the tensile strength of neat epoxy (100% epoxy) was not investigated. Review literature shows divergent findings with some reporting that neat epoxy have higher tensile strength compared to fish scale reinforced composites [44,48,52]. On the other hand, a study by [46] has reported enhanced tensile strength with incorporation of fish scales.

Similarly, other researchers [45,47,52] have concluded that flexural properties increases with fish scale loading. For example, [45], reported increase in flexural strength as catla fish scale in the composite increased from 10 wt% to 30 wt%. The study observed that as fish scale content increased, there was excellent distribution and dispersion of fillers in the matrix thus improving the stiffness and rigidity of the resultant composite [45]. This prevented flexural deformation of the specimen hence the increase in flexural strength with filler loading. Additionally, this caused the flexural strength of the reinforced composites to be higher than that of neat epoxy. Further, a research by [47] reported increase in flexural strength with fish scale volume fraction to attain maximum flexural strength at 30 vol%. The study attributed this trend to uniform dispersion and distribution of fish scale fillers in the matrix. However, weak interfacial bonding between the filler and matrix as well as agglomeration caused reduction of flexural strength at higher filler content. In addition, other studies [48,52,64] showed negligible increase in flexural strength with increase in fish scale loading. The high amount of protein fish scale structure prevents interaction between starch matrix and fish scale hence insignificant increase in flexural strength with addition of fish scale reinforcement [64]. In another study by [38] on characterization and biodegradability of polypropylene composites from agricultural residues and waste fish reported decrease in flexural properties as waste fish content in the composite increased from 0% to 15%.

In contrast, [47] reported marginal increase in impact strength of fish scale reinforced epoxy composites with increase in fish scale filler. The impact strength increased marginally due to brittleness of the composites to attain maximum impact strength of 5.5 J at 25 vol% filler proportion. Further increase in filler content beyond 25 vol% resulted into agglomeration thus reducing the filler-matrix interfacial bonding hence decreased impact strength of the composites. Similarly, a research by [48] reported improvement of the resistance to impact loading of the fish scale reinforced epoxy composites. On the other hand, a study by [65] reported increase in impact strength with fish scale loading up to 10%, increasing the percentage of fish scale further reduced the impact strength. In addition, a study by [66] on fish scale-cellular composite system for protection against low-velocity impact concluded that the presence of fish scales in the composites prevented the penetration of the impact hammer. The scales in the composites deformed plastically forming plastic hinges thus dissipating higher energy as they deformed.

5. CONCLUSIONS

Fish scales with minimal or no economic value can be used as biodegradable reinforcement for biocomposites fabrication. Additionally, bioplastics can be extracted from fish scale wastes thus adding value to these wastes. The properties of fish scale bioplastics are greatly influenced by environmental conditions such as temperatures which influence imino acids composition. Several studies have concluded that the content of hydroxyproline imino acid content is dependent on the environmental temperatures in which the fish lives. Besides imino acids, other studies have reported that some fish collagen contain higher glycine content. However, not much research has been conducted on the effect of glycine on physiochemical, functional and rheological properties of the resultant biopolymer. Although fish scales have been used as reinforcement for biocomposites fabrication, its effects on mechanical properties of the resultant biocomposites is divergent. Also, there is a gap in knowledge on the use of bioplastics extracted from fish scales for biocomposites fabrication as well as the effect of bioplastics properties of mechanical properties of resultant biocomposites.

6. ACKNOWLEDGEMENTS

This research work was supported by Vaal University of Technology. The authors wish to thank the department of Mechanical Engineering at Vaal University of Technology for facilitating this work.

REERENCES

1. Rhim J-W, Ng PKW. Natural Biopolymer-Based Nanocomposite Films for Packaging Applications. Crit Rev Food Sci Nutr. 2007 Apr 26;47(4):411–33.
2. Limpan N, Prodpran T, Benjakul S, Prasarpran S. Influences of degree of hydrolysis and molecular weight of poly(vinyl alcohol) (PVA) on properties of fish myofibrillar protein/PVA blend films. Food Hydrocoll. 2012 Oct 1;29(1):226–33.
3. Zavareze E da R, Halal SLME, Silva RM e, Dias ARG, Prentice‐ Hernández C. Mechanical, Barrier and Morphological Properties of Biodegradable Films Based on Muscle and Waste Proteins from the Whitemouth Croaker (Micropogonias furnieri). J Food Process Preserv. 2014;38(4):1973–81.
4. Harnedy PA, Fitzgerald RJ. Bioactive Proteins and Peptides from Macroalgae, Fish, Shellfish and Marine Processing Waste. In: Marine Proteins and Peptides (Internet). John Wiley & Sons, Ltd; 2013 (cited 2020 Aug 5). p. 5–39. Available from: https://onlinelibrary.wiley.com/doi/abs/10.1002/9781118375082.ch2
5. Artharn A, Benjakul S, Prodpran T. The effect of myofibrillar/sarcoplasmic protein ratios on the properties of round scad muscle protein based film. Eur Food Res Technol. 2008 May;227(1):215–22.
6. Rumengan IFM, Suptijah P, Wullur S, Talumepa A. Characterization of chitin extracted from fish scales of marine fish species purchased from local markets in North Sulawesi, Indonesia. IOP Conf Ser Earth Environ Sci. 2017 Oct 1;89(1):1–5.
7. Araújo C da S, Rodrigues A, Joele MRSP, Araujo EAF, Lourenço L de FH. Optimizing process parameters to obtain a bioplastic using proteins from fish byproducts through the response surface methodology. Food Packag Shelf Life. 2018;16:23–30.
8. Wangtueai S, Noomhorm A. Processing optimization and characterization of gelatin from lizardfish (Saurida spp.) scales. LWT - Food Sci Technol. 2009 May 1;42(4):825–34.
9. Gennadios A. Protein-based films and coatings. CRC press; 2002.
10. Olatunji O, Igwe CC, Ahmed AS, Alhassan DOA, Asieba GgO, Diganta BD. Microneedles from fish scale biopolymer. J Appl Polym Sci (Internet). 2014 (cited 2020 Aug 3);131(12). Available from: https://onlinelibrary.wiley.com/doi/abs/10.1002/app.40377
11. Suptijah P, Indriani D, Wardoyo dan SE. Isolation and Characterization of Collagen from the Skin of Catfish (Pangasius sp.). J Sains Nat Univ Nusa Bangsa. 2018 Jan;8(1):8–23.
12. Jongjareonrak A, Benjakul S, Visessanguan W, Tanaka M. Skin gelatin from bigeye snapper and brownstripe red snapper: Chemical compositions and effect of microbial transglutaminase on gel properties. Food Hydrocoll. 2006 Dec;20(8):1216–22.

13. Ninan G, Jose J, Abubacker Z. Preparation and Characterization of Gelatin Extracted from the Skins of Rohu (labeo Rohita) and Common Carp (cyprinus Carpio). J Food Process Preserv. 2011;35(2):143–62.
14. Muyonga JH, Cole CGB, Duodu KG. Characterisation of acid soluble collagen from skins of young and adult Nile perch (Lates niloticus). Food Chem. 2004 Mar 1;85(1):81–9.
15. Ikoma T, Kobayashi H, Tanaka J, Walsh D, Mann S. Physical properties of type I collagen extracted from fish scales of Pagrus major and Oreochromis niloticas. Int J Biol Macromol. 2003b;32(3–5):199–204.
16. Chai H-J, Li J-H, Huang H-N, Li T-L, Chan Y-L, Shiau C-Y, et al. Effects of Sizes and Conformations of Fish-Scale Collagen Peptides on Facial Skin Qualities and Transdermal Penetration Efficiency. J Biomed Biotechnol. 2010;2010:1–9.
17. Kasankala LM, Xue Y, Weilong Y, Hong SD, He Q. Optimization of gelatine extraction from grass carp (Catenopharyngodon idella) fish skin by response surface methodology. Bioresour Technol. 2007 Dec;98(17):3338–43.
18. Moss ML, Jones SJ, Piez KA. Calcified Ectodermal Collagens of Shark Tooth Enamel and Teleost Scale. Science. 1964 Aug 28;145(3635):940–2.
19. Jongjareonrak A, Benjakul S, Visessanguan W, Nagai T, Tanaka M. Isolation and characterisation of acid and pepsin-solubilised collagens from the skin of Brownstripe red snapper (Lutjanus vitta). Food Chem. 2005 Dec 1;93(3):475–84.
20. Gilsenan P, Ross-Murphy SB. Rheological characterisation of gelatins from mammalian and marine sources. Food Hydrocoll. 2000 May;14(3):191–5.
21. Gómez-Guillén MC, Turnay J, Fernández-Dı́az MD, Ulmo N, Lizarbe MA, Montero P. Structural and physical properties of gelatin extracted from different marine species: a comparative study. Food Hydrocoll. 2002 Jan;16(1):25–34.
22. Mahboob S. Isolation and characterization of collagen from fish waste material- skin, scales and fins of Catla catla and Cirrhinus mrigala. J Food Sci Technol. 2015 Jul;52(7):4296–305.
23. Zhang Y, Liu W, Li G, Shi B, Miao Y, Wu X. Isolation and partial characterization of pepsin-soluble collagen from the skin of grass carp (Ctenopharyngodon idella). Food Chem. 2007 Jan;103(3):906–12.
24. Giraud-Guille M-M, Besseau L, Chopin C, Durand P, Herbage D. Structural aspects of fish skin collagen which forms ordered arrays via liquid crystalline states. Biomaterials. 2000 May;21(9):899–906.
25. Nagai T, Izumi M, Ishii M. Fish scale collagen. Preparation and partial characterization. Int J Food Sci Technol. 2004;39(3):239–244.
26. Ogawa M, Moody MW, Portier RJ, Bell J, Schexnayder MA, Losso JN. Biochemical Properties of Black Drum and Sheepshead Seabream Skin Collagen. J Agric Food Chem. 2003 Dec;51(27):8088–92.
27. Kittiphattanabawon P, Benjakul S, Visessanguan W, Nagai T, Tanaka M. Characterisation of acid-soluble collagen from skin and bone of bigeye snapper (Priacanthus tayenus). Food Chem. 2005 Feb;89(3):363–72.
28. Kimura S, Zhu X-P, Matsui R, Shijoh M, Takamizawa S. Characterization of Fish Muscle Type I Collagen. J Food Sci. 1988 Sep;53(5):1315–8.
29. Grossman S, Bergman M. PROCESS FOR THE PRODUCTION OF GELATIN FROM FISH SKINS. 5,093,474, 1992. p. 1–8.
30. Gudmundsson M, Hafsteinsson H. Gelatin from cod skins as affected by chemical treatments. J Food Sci. 1997 Jan;62(1):37–9.
31. Poppe J. Gelatin. In: Imeson A, editor. Thickening and Gelling Agents for Food (Internet). Boston, MA: Springer US; 1992 (cited 2020 Aug 8). p. 98–123. Available from: http://link.springer.com/10.1007/978-1-4615-3552-2_5
32. Ismail N, Shukor N, Samicho Z. Effects of extraction time on the functional properties of silver catfish (Pangasius sutchi) skin gelatin. Sci Res J. 2013;10(1):65–81.
33. Badii F, Howell N. Fish gelatin: Structure, gelling properties and interaction with egg albumen proteins. Food Hydrocoll. 2006 Jul;20(5):630–40.
34. Yang J-I, Ho H-Y, Chu Y-J, Chow C-J. Characteristic and antioxidant activity of retorted gelatin hydrolysates from cobia (Rachycentron canadum) skin. Food Chem. 2008 Sep;110(1):128–36.
35. Sims TJ, Avery NC, Bailey AJ. Quantitative Determination of Collagen Crosslinks. In: Extracellular Matrix Protocols (Internet). New Jersey: Humana Press; 2000 (cited 2020 Aug 3). p. 11–26. Available from: http://link.springer.com/10.1385/1-59259-063-2:11
36. Monterrey-Quintero ES, Sobral PJ do A. Preparo e caracterização de proteínas miofibrilares de tilápia-do-nilo para elaboração de biofilmes. Pesqui Agropecuária Bras. 2000 Jan;35(1):179–89.
37. Zhu D, Barthelat F, Vernereyb F. Intricate Multiscale Mechanical Behaviors of Natural Fish-Scale Composites. Handb Micromechanics Nanomechanics Ed Li X Gao. 2013;975–98.
38. Nourbakhsh A, Ashori A, Tabrizi AK. Characterization and biodegradability of polypropylene composites using agricultural residues and waste fish. Compos Part B Eng. 2014;56:279–283.
39. Prasad A, Bhasney SM, Sankar MR, Katiyar V. Fish scale derived hydroxyapatite reinforced poly (lactic acid) polymeric bio-films: possibilities for sealing/locking the internal fixation devices. Mater Today Proc. 2017;4(2):1340–1349.
40. Kumar S, Verma T, Khatri B, umar A, Patel VK. BIO-WASTES (FISH SCALE AND PINE CONE) BASED HYBRID POLYMER COMPOSITES FOR TRIBOLOGICAL APPLICATIONS. Asian J Sci Technol. 2017;08(03):4489–92.
41. Kumar A, Bansal G, Singh VK. Characterization of

Mechanical Strength of Epoxy Hybrid Composite Reinforced with Chicken Feather Fiber and Residue Powder Extracted from Rohu Fish Scale. Int J Eng Res Technol IJERT ISSN. 2019;2278–0181.

42. Dixit S, Verma P. The effect of hybridization on mechanical behaviour of coir/sisal/jute fibres reinforced polyester composite material. Res J Chem Sci ISSN. 2012;2231:606X.
43. Dan-Mallam Y, Abdullah MZ, Yusoff PSMM. The effect of hybridization on mechanical properties of woven kenaf fiber reinforced polyoxymethylene composite. Polym Compos. 2014;35(10):1900–1910.
44. Razi ZM, Islam MR, Parimalam M. Mechanical, structural, thermal and morphological properties of a protein (fish scale)-based bisphenol-A composites. Polym Test. 2019;74:7–13.
45. Aradhyula TV, Bian D, Reddy AB, Jeng Y-R, Chavali M, Sadiku ER, et al. Compounding and the mechanical properties of catla fish scales reinforced-polypropylene composite–from biowaste to biomaterial. Adv Compos Mater. 2019;29(2):115–128.
46. Thammahiwes S, Riyajan S-A, Kaewtatip K. Preparation and properties of wheat gluten based bioplastics with fish scale. J Cereal Sci. 2017;75:186–191.
47. Babu KR, Jayakumar V, Bharathiraja G, Madhu S. Experimental investigation of fish scale reinforced polymer composite. Mater Today Proc. 2020;22:416–418.
48. Satapathy A, Patnaik A, Pradhan MK. A study on processing, characterization and erosion behavior of fish (Labeo-rohita) scale filled epoxy matrix composites. Mater Des. 2009;30(7):2359–2371.
49. Majhool AA, Zainol I, Azziz SSSA, CN AJ. Mechanical properties improvement of epoxy composites by natural hy-droxyapatite from fish scales as a fillers. Int J Res Pharm Sci. 2019;10(2):1424–1429.
50. Oladele IO, Akinola OS, Agbabiaka OG, Omotoyinbo JA. Mathematical Model for the Prediction of Impact Energy of Organic Material Based Hydroxyapatite (HAp) Reinforced Epoxy Composites. Fibers Polym. 2018;19(2):452–459.
51. Selvin TP, Kuruvilla J, Sabu T. Mechanical properties of titanium dioxide-filled polystyrene microcomposites. Mater Lett. 2004;58(3–4):281–289.
52. Satapathy A, Pradhan MK, Mishra D, Patnaik A. Fabrication, Mechanical Characterization and FTIR Spectroscopic Analysis of Fish Scale Reinforced Epoxy Composites. In: Advanced Materials Research. Trans Tech Publ; 2012. p. 889–892.
53. Pang S, Chang YP, Woo KK. The Evaluation of the Suitability of Fish Wastes as a Source of Collagen. In: 2nd International Conference on Nutrition and Food Sciences. Singapore: IACSIT Press; 2013. p. 77–81.
54. Muralidharan N, Jeya Shakila R, Sukumar D, Jeyasekaran G. Skin, bone and muscle collagen extraction from the trash fish, leather jacket (Odonus niger) and their characterization. J Food Sci Technol. 2013 Dec 1;50(6):1106–13.
55. Nagai T, Suzuki N. PREPARATION AND CHARACTERIZATION OF SEVERAL FISH BONE COLLAGENS. J Food Biochem. 2000 Oct;24(5):427–36.
56. Duan R, Zhang J, Du X, Yao X, Konno K. Properties of collagen from skin, scale and bone of carp (Cyprinus carpio). Food Chem. 2009;112(3):702–706.
57. Sadowska M, Kolodziejska I, Niecikowska C. Isolation of collagen from the skins of Baltic cod (Gadus morhua). Food Chem. 2003;81(2):257–262.
58. Tabarestani HS, Maghsoudlou Y, Motamedzadegan A, Mahoonak AR, Rostamzad H. Study on some properties of acid-soluble collagens isolated from fish skin and bones of rainbow trout (Onchorhynchus mykiss). Int Food Res J. 2012;19(1):251–7.
59. Rigby BJ. Amino-acid composition and thermal stability of the skin collagen of the Antarctic ice-fish. Nature. 1968;219(5150):166–167.
60. Bae I, Osatomi K, Yoshida A, Osako K, Yamaguchi A, Hara K. Biochemical properties of acid-soluble collagens extracted from the skins of underutilised fishes. Food Chem. 2008;108(1):49–54.
61. Zhang F, Wang A, Li Z, He S, Shao L. Preparation and Characterisation of Collagen from Freshwater Fish Scales. Food Nutr Sci (Internet). 2011 (cited 2020 Aug 3); Available from: https://agris.fao.org/agris-search/search.do?recordID=DJ2012073266
62. Kim S-K, Mendis E. Bioactive compounds from marine processing byproducts–a review. Food Res Int. 2006;39(4):383–393.
63. Monterrey-Quintero ES, Sobral PJ do A. Preparo e caracterização de proteínas miofibrilares de tilápia-do-nilo para elaboração de biofilmes. Pesqui Agropecuária Bras. 2000 Jan;35(1):179–89.
64. Chiarathanakrit C, Riyajan S-A, Kaewtatip K. Transforming fish scale waste into an efficient filler for starch foam. Carbohydr Polym. 2018;188:48–53.
65. Gopi V, Clement Arun S, Gopi A, Sankaranarayanan S, Stephen Raj S. Characterization of Fish Scale Reinforced Composites. Int J Eng Sci Comput. 2016;06(05):5227–30.
66. Chua YS, Law E, Dai Pang S, Quek ST. Fish scale-cellular composite system for protection against low-velocity impact. Compos Struct. 2016;145:217–225.