

ANIMAL PROTEIN BIOPLASTICS

Abstract

Plastic and resulting environmental pollution is the well debated talk of today's scenario. We all are dependent on plastics for daily activities and this is the reason why we continue to use it even after being well acquainted with the environmental threats that it poses. While looking for alternatives to synthetic plastic, bioplastics are the material of the future. The bioplastics are formed from natural materials like polyesters, carbohydrates and proteins among others. These bioplastics are biodegradable hence are not detrimental to the natural ecosystem. This chapter discusses in detail the bioplastics made up of different animal protein sources, their physicochemical properties and their potential applications.

Keywords: Bioplastics, protein, biodegradable, biofilms, collagen, keratin

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The usage of synthetic plastics is expanding in last few years and our dependence on it for the day to day life cannot be ignored. Synthetic plastics are the material of choice to make daily use products owing to their physiochemical, mechanical properties and their ability to be molded and extruded in a variety of ways. Although of great use, synthetic plastics are the biggest threat to the environment because of their non biodegradable nature. The non biodegradability of plastics makes them the causative agent of environmental pollution and climate change. Plastics are accumulating in water ecosystems as each year millions of tons of plastic waste, including micro and macro debris enters into lakes, ponds and oceans. This debris is life threatening hazard for marine creatures like fish, turtle, and tortoise among many others. Many studies have reported the presence of nano plastics inside the bodies of fishes, shrimps and lobsters. Consuming the contaminated seafood or water also poses serious threat to human health. In fact latest studies by Heather A. Leslie, Amsterdam University in 2022 have shown the presence of plastics such as Polyethylene tetra phthalate, polyethylene, Polystyrene in human blood [1]. Mean quantity of 1.6 $\mu\text{g/ml}$ of plastic particles has been reported by the researchers. An estimated increase of 40% is expected by the year 2025 to Asia Pacific Coral Reefs [2].

Combating the problem of plastic pollution has been sought by various methods including chemical degradation and/ or recycling. Chemical degradation leads to an incomplete degradation of plastics and also results in the release of toxic gases, so it is not a favorable alternative. Other alternates include pyrolysis, catalytic and enzymatic degradation which have their own limitations. In order to tackle the above mentioned issues, plastics can be produced from biopolymers or polyesters that are safer for both environment and mankind. Various sources of biopolymers suitable for the production of bioplastics include polyesters, proteins and carbohydrates. Bioplastics are suitable alternatives as they are biodegradable and have promising mechanical properties.

This chapter will cover the proteins from various animal sources that are currently being explored by researchers for the production of bioplastics. Proteins can serve as an excellent source of various functional groups present in their side chains that could participate in the formation of intermolecular bonds. The steps involved in the preparations of protein based bioplastics include denaturing, cross-linking and plasticization. The above properties make protein a promising candidate for the preparation of bioplastics of the future. (Fig 1.)

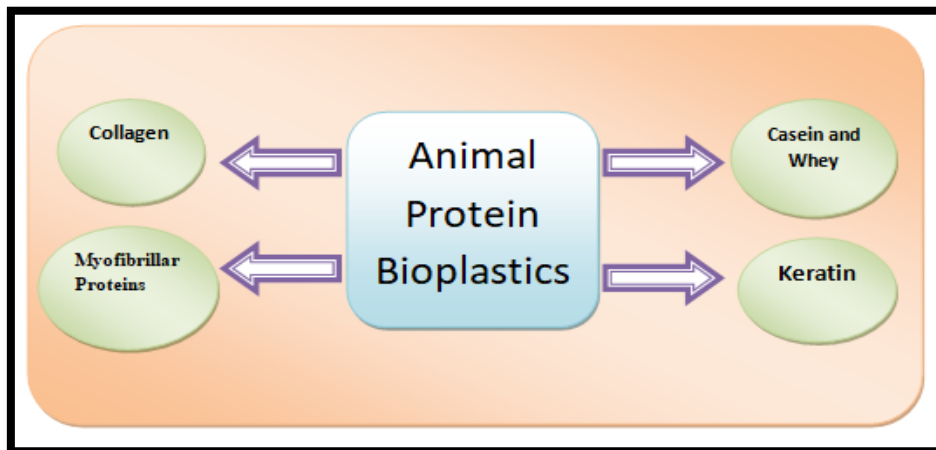


Figure 1: Animal Protein sources of Bioplastics

- Collagen:** Collagen protein is animal protein present in bone, muscle, skin and blood vessels of mammals. It is the most abundant protein in our body representing one-third of the total protein component. In vertebrates, a total of twenty-six different types of collagen made up of forty-six different polypeptide chains are present[3]. Collagen has the ability to self assemble under laboratory conditions, in a solution to form aggregates employing the intermolecular attraction forces. Collagen bioplastics have been formed by the process of extrusion alone and in combinations with other material in order to improve the physical properties of the films (Fig. 2).[Table1]

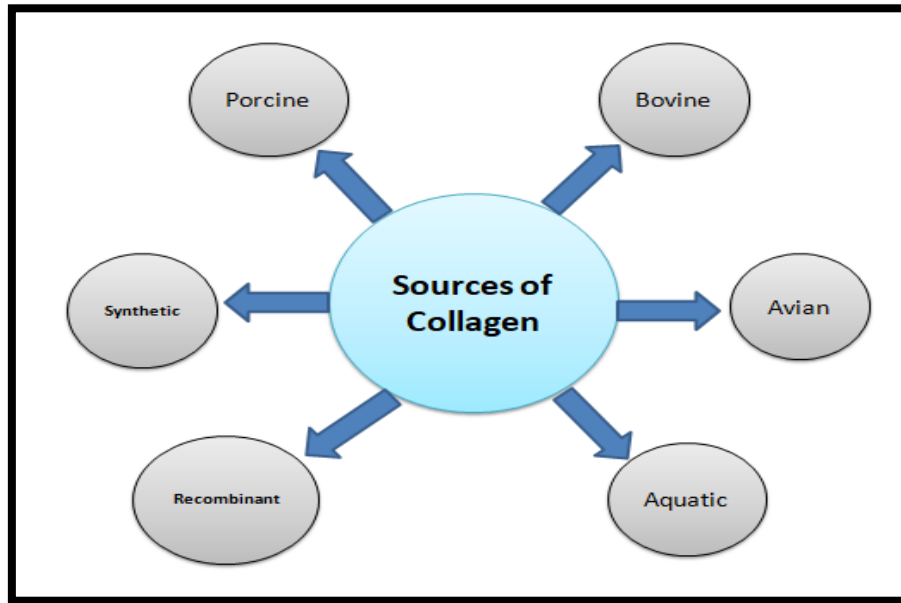


Figure 2: Sources of Collagen

Table 1: Collagen Bioplastics

Sl.no	Composition	Properties	Applications	Reference
1	Collagen and Starch	The films composed of starch and collagen were reported to possess' rough surface as compared to the pure collagen films. The former was reported to become smoother upon heat treatment. The authors have reported improved tensile strength than the pure collagen films in both wet and dry state upon heat treatment. Addition of starch also resulted in improved thermal stability. Heating also resulted in increased intermolecular interactions between starch and collagen.	Biodegradable Packaging	[4]
2	Transglutaminase crosslinked Collagen	The researchers reported a decrease in film thickness and increase in thermal stability of the collagen films upon cross linking with TGase at 45 °C and 65 °C.	Biodegradable and Edible packaging	[5]

3	Collagen , Soy Protein and NaCl	Addition of NaCl resulted in higher tensile strength and elasticity in the films. Addition of soy protein alone decreased gel and film properties whereas soy protein and NaCl together produced better film properties.	Food and Pharmaceutical industry	[6]
4	Collagen and Polycaprolactone	Collagen biopolymeric fibers with PCL depicted increased tensile strength.	Drug delivery, Enzyme immobilization and Advanced Biomedical Applications	[7]

2. Myofibrillar Proteins: These proteins involve actin and myosin components of the skeletal muscle of animals. The Myofibrillar proteins from fish and chicken have been reported for the formation of edible films [8] [9]. The myofibrillar bioplastic films with different combinations are summarized in Table2. The fish waste has also been used for the formation of bioplastics (Fig3)



Figure 3: Bioplastic from fish waste .Ref [14]

Table 2: Myofibrillar Bioplastics

Sl. no	Composition	Properties	Applications	Reference
1	Myofibrillar Proteins and Microbial Transglutaminase	More compact and homogeneous film structure, improved mechanical properties, tensile strength and water vapour permeability. These films exhibited decreased solubility.	Edible Films	[10] [11]
2	mTGase modified Fish myofibrillar Protein and Montmorillonite (MMT) nano clay	Improved water gain, water vapor permeability, and solubility of the films are reported by the researchers	Packaging Biofilms, Nanocomposites	[12]
3	Crayfish Flour with Sodium sulphite/Urea	Increased torque value upon SS and Urea addition	biodegradable plastic materials	[13]
4	Fish byproduct	Myofibrillar films from fish byproduct with plasticizers (40%) have been reported to possess homogenous, translucent, resistant and flexible properties. These bioplastics exhibit low water solubility and water vapour permeability	Food packaging	[14][15]
5	Fish byproduct and passion fruit pectin	Optimum films were formed with 5% protein and 3% pectin. The films exhibited better thermal properties and biodegradability.	Food packaging	[16]

3. Milk Proteins: The major components of milk include: water, fat, protein, lactose and minerals. The proteins present in milk are casein and whey. Protein constitutes approximately 3.5% of bovine milk, with slight variations within different breeds.

- **Casein:** Casein is present only in milk and is present in the form of calcium caseinate-phosphate complex. It forms more than 8% of the total protein component of milk and is present in the colloidal state. Casein is composed of three separate fractions viz. α , β and γ in the form of micelle. The casein isolated from bovine milk has been studied for the formation of bioplastics films as summarized in Table 3 (Fig 4).

Figure 4: SEM Images of casein gelatin composite film [19]

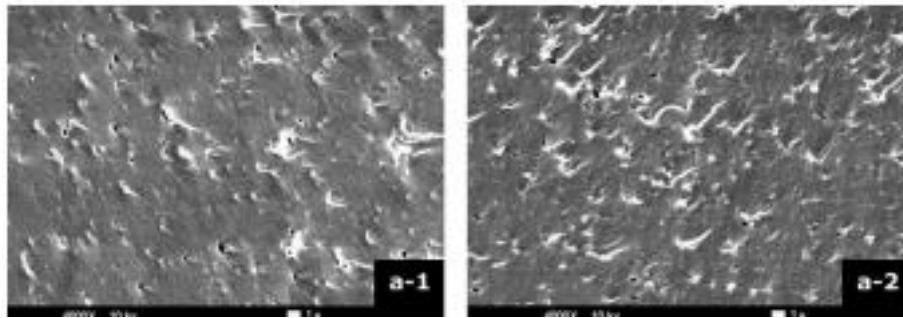


Table 3: Casein Bioplastics

Sl.no	Composition	Properties	Applications	Reference
1	Casein Phosphopeptides (CPP) and gelatin films	Addition of CPP resulted in a decrease in water solubility, water vapour activity and light transmittance of the gelatin films as stated by the authors. The composite films exhibited good tensile properties. Lower concentrations of CPP (approximately 0.1-0.2%) is reported to be the most suitable.	Food packaging	[17]
2	Starch and Casein	The researchers reported antimicrobial properties against E. coli, Staphylococcus aureus, Bacillus cereus, Listeria monocytogenes, Pseudomonas spp., and Salmonella of starch- casein edible films in the presence or absence of neem. It was also found out that the heat pressing resulted in decrease in water vapour transmissibility rate and slight change in oxygen transmission rate. Heating lead to toughening of the edible film with improved tensile properties.	Breathable films for MAP (modified atmosphere packaging)	[18]
3	Casein and gelatin cross-linked with Transglutaminase	The authors have reported the formation of casein and gelatin films alone and as blends , modified by transglutaminase. The blend films were reported to have greater elongation values compared to the pure casein or gelatin films. There was no effect on the tensile and water barrier properties of the film in the blends although except casein: gelatin (75:25) formulation which is reported to possess lowest WVPV. (Fig.3)	Edible Films	[19]
4	Sodium Caseinate	Glycerol is reported to be more effective as plasticizer then sorbitol in the sodium caseinate films. Films with 90% sorbitol had comparable tensile properties with 40-50% glycerol. Oleic acid and beeswax have also been reported to have plasticizing effects and improved elasticity, flexibility and stretchability, and reduces water vapor permeability of these films as stated by the authors.	Edible Films	[20], [21]

- **Whey:** β - lactoglobulins and α - lactalbumin constitute the whey proteins or serum proteins of milk. These proteins are present in the colloidal form and can be easily heat coagulated. These proteins have found to possess an excellent film forming properties [23]. Films based on whey proteins have good flexibility, transparency and gas barrier properties (Fig 5). Various whey protein based films that are studied have been summarized in Table4.

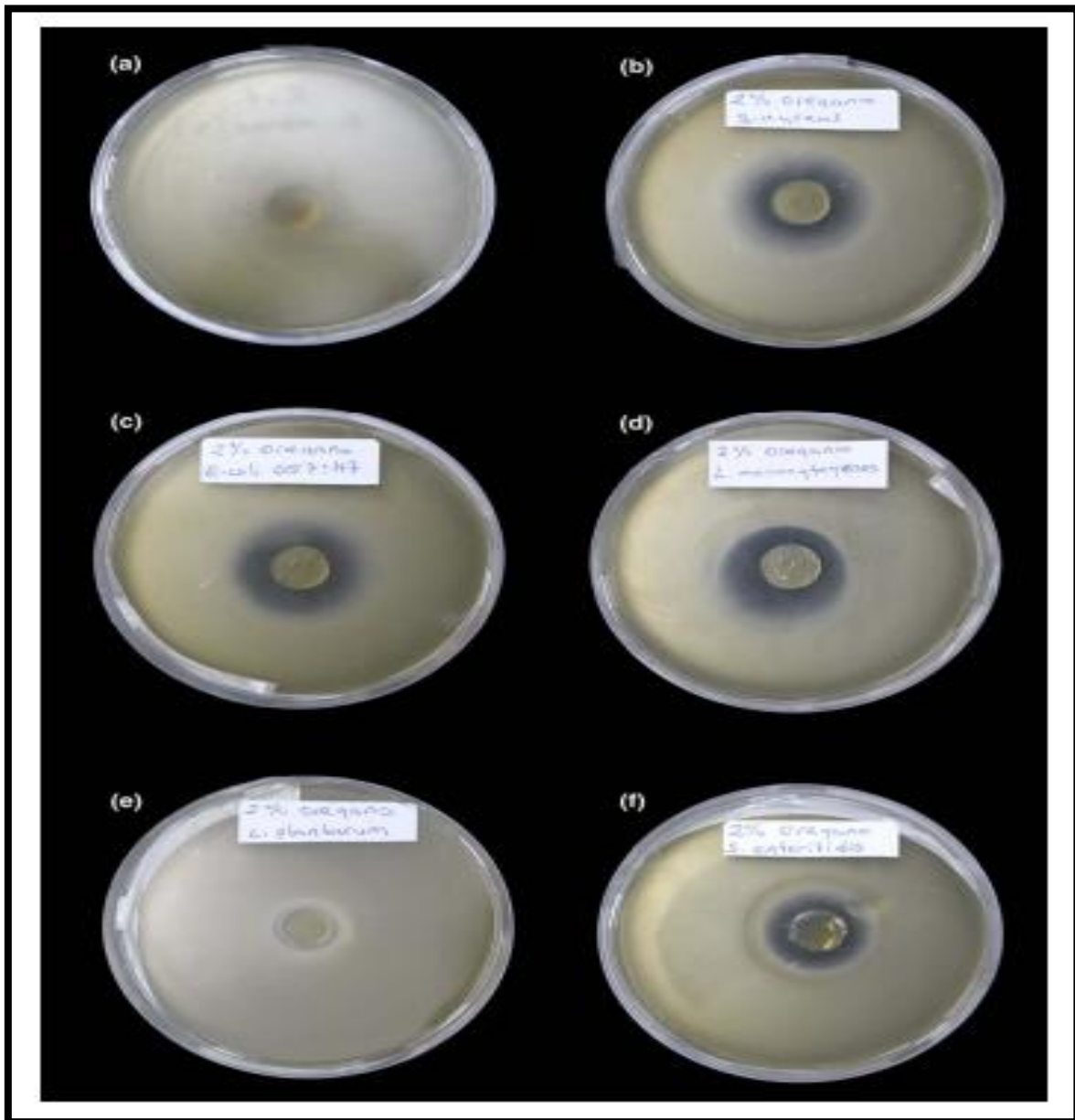


Figure 5: Inhibitory zones of WP films with 2% oregano essential oils [26]

Table 4: Whey Protein Biofilms

Sl no.	Composition	Properties	Applications	Reference
1	Whey Protein	Whey Protein films formed by ultrasonic treatment have slightly less water vapour permeability than the films produced by heat treatment. Ultrasound also improved tensile and puncture properties of the films. Although heat treated films are reported to possess better mechanical and tensile properties, thus better suitable for cheese slice separation material.	Cheese Slice Packaging	[22],[23]
2	Whey Protein Concentrate (WPC)	Formation of WPC films by casting in the presence of glycerol and sorbitol has been reported. Film thickness increased from 0.168 to 0.305mm (with glycerol) and from 0.251 to 0.326 mm (with sorbitol) with maximum plasticizer concentrations.	Cheddar Cheese Packaging	[24],[25]
3	Whey Protein and Essential Oils	Antimicrobial properties of oregano, rosemary and garlic essential oils incorporated in whey protein edible films have been reported. Among all these, oregano essential oil is reported to be most effective (at concentration of 2%). Although WP films showed poor water barrier properties but it was improved by incorporation of essential oils.	Active Packaging	[26],[27]
4	WPI and Pullulan	WPI and pullulan films in different ratios were formed and it was found that pullulan at low concentrations was effective in improving the properties of Whey Protein films	Food packaging	[28]
5	WPI and Gluconal Cal (mixture of calcium lactate and gluconate/α-tocopheryl acetate (VE)	Addition of Gluconal Cal and α -tocopheryl acetate resulted in increased film elongation at break	Wrapping or coating to enhance the nutritional value of foods.	[29]

4. Keratin: Keratin is a fibrous protein present in hair, horns, feathers, nails of animals. Human hair is 80% keratin and chicken feather is almost 90% keratin. The keratinous materials are often discarded as waste. The keratin from sheep wool, chicken feather waste and human hair can be used for the production of bioplastics. The Hydrogels, films and fibers produced have been known for various biomedical applications like wound healing, autonomous nerve regeneration, drug delivery systems among others. Table 5 summarizes various bioplastics based on keratin from various sources (Fig6).

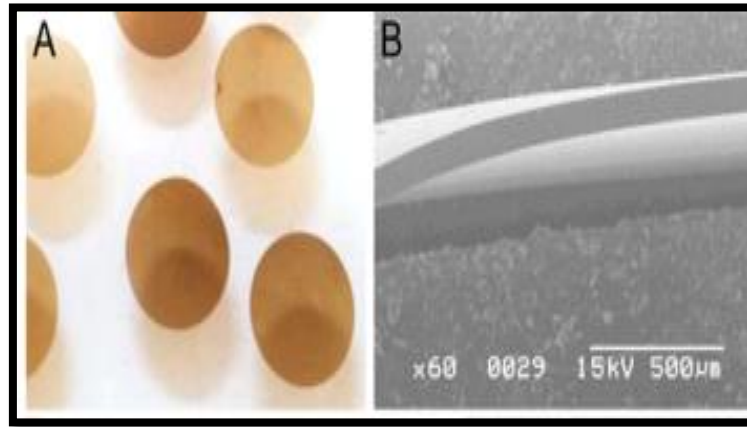


Figure 6: Keratin Bioplastic and its SEM image [30]

Table 5: Keratin Bioplastics

Sl no	Composition	Properties	Applications	Reference
1	Aqueous and alkaline keratin dialysate	Glycerol used as plasticizer at 1% concentration followed by curing of the films at 100 °C for 2 hrs.	Epithelial Wound Healing , Ocular Surface reconstruction	[30], [31]
2	Keratin Crosslinked with TGase	Treatment with TGase improved the tensile strength and decreased the elongation break of the keratin films. Authors have also reported an improved film stability in gastric juice and PBS. Although these films showed rougher surface but presence of higher molecular weight proteins as a result of crosslinking is seen.	Tissue Engineering	[32]
3	Keratin, chitosan/ gelatin	Improved Water uptake properties and porosity, thermal and physical stability has been reported by the authors . The scaffolds have shown biocompatibility	Tissue Engineering and wound healing	[33],[34],[35]
4	Keratin and Polyvinyl alcohol(PVA)	Authors have reported formation of nano fibers by electrospinning with higher mechanical strength and thermal stability.	Nano Fibers	[36]
5	Keratin hydrogel	Sheep wool keratin used with glycerol as plasticizer for the generation of hydrogel	Differentiation of odontoblast-like cells for pupal regeneration	[37]

CONCLUSION

Owing to the cross linking and biodegradable nature of proteins, these can effectively be used for the preparation of bio based plastics. These plastics have found diverse applications, including food packaging, wrapping, edible films from milk based and collagen proteins. The keratin based biomaterials have found utilization in various biomedical applications. Therefore, to summarize, in order to combat the environmental problems being faced by extensive use of petroleum based plastics, proteins from animal sources can serve as an excellent material for production of bio based plastics.

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