INVESTIGATION OF MECHANICAL PROPERTIES OF CHITOSAN BASED FILMS PREPARED FROM NARMADA RIVERSIDE CRAB SHELLS

Dr. K. K. Gadghey

Head, Department of Mechanical Engineering,
Government Polytechnic College, Sanawad, Madhya Pradesh, India

Dr. G. S. Sharma

Professor and Head, Department of Mechanical Engineering,
Oriental University, Indore, Madhya Pradesh, India

ABSTRACT

The aim of this investigation is to enhance the utilization of crab waste and help to minimize the environmental pollution. The Narmada riverside crab shells were collected and Chitosan based films prepared. The tensile tests were performed to investigate tensile strength and elongation at break. The tensile strength of pure chitosan films was found to be 122.6 MPa and the elongation at break 13.6% with film thickness 0.110 mm. The films were plasticized with different percentage of glycerol and the values of film thickness, elongation at break and tensile strength were analyzed. The tensile strength decreased with the increase in glycerol. Film thickness and elongation at break increased with increase in glycerol. The tensile strength of prepared films showed better results compared to previous results of chitosan based films prepared from other sources.

Keywords: Biopolymer, Chitin, chitosan, Crab shell, Narmada Riverside

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1. INTRODUCTION

The food processing industries produce many by-products. The treatment of the waste produced can help in saving the environment. This waste can turn into useful and valuable products. The crab shells contain chitin, polysaccharides that can be extracted by chemical and biological processes. This biopolymer and its derivative chitosan have many useful applications. Compared to polymeric resources from petroleum, natural polymers from

renewable resources have the advantages of biodegradability, biocompatibility, non-toxicity, high reactivity, low cost and ease of availability. Narmada riverside crabs are not known to researchers. The quality and quantity of Narmada riverside crab shells or crab waste is not recognized till date. There is no recognized crab industry in India like other countries of the world. Green Technology is a pretty new concept in respect to the environment protection timeline. It is all about the best ways and methods that preserve our natural resources and sustainability of life on our planet earth. It is important to bring technological change for promoting green growth with reduced cost [1]. Biopolymers are polymers produced by living organisms. Bio based plastics and biopolymers have been widely studied in recent years. Replacing the oil-based packaging materials with bio based films and containers might give not only a competitive advantage due to more sustainable and greener image, but also some improved technical properties [2]. Chitin is the second most abundant natural polymer in nature after cellulose [3]. Chitin and its derivatives chitosan have several applications, these include, biomedical, food, emulsifying agent, wastewater treatment, biocatalysts, textile and paper industry and agriculture [4]. It is found in exoskeleton of crustaceans. Crab shell is the most common natural composite material in the world, and one of the most versatile. Very few mechanical studies have been made on the hard shells (solid cuticle) characteristic of the arthropod integument and it is therefore not yet possible to provide a general model for the mechanical behavior of the exoskeletons of this phylum. The exoskeleton of arthropods consists mainly of chitin. In the case of crustaceans, there is a high degree of mineralization, typically calcium carbonate, which gives mechanical rigidity. The various studies have been carried out on insect solid cuticle [5-9] and prawn shells [10]. The arthropod exoskeleton is multifunctional: it supports the body, resists mechanical loads, and provides environmental protection and resistance to desiccation [11–15]. Chitin is a substance that makes up the exoskeleton of insects and crustaceans, which can also be obtained from other sources like fungi, mushrooms, worms, diatoms, etc[16-19]. Chitin and its derivatives chitosan have several applications, these include, biomedical, food, emulsifying agent, waste Chitosan is a natural polysaccharide derived from chitin. The low solubility of chitin derived chitosan in neutral and alkaline solution limits its application. Therefore, the chemical modification into composites and blends brings it into new important functional properties for different engineering applications. It is recognized as versatile biomaterials because of its non-toxicity and biocompatibility. These waste crab shells can be utilized to prepare chitin and chitosan. The extraction of chitin can be done by chemical and biological methods. The crab shell contains chitin, protein and minerals. The deproteinization and demineralization are the main processes to extract chitin from crab shells. The deacetylation of chitin is done to prepare the chitosan which is the important biopolymer to be used mostly in biomedical applications. The chitosan has good film forming capability hence it can replace the polythene bags from the market. It is necessary to know the mechanical strength of the prepared biopolymer. The chitin so produced can be utilized in many applications but there is one important limitation in its utilization, the mechanical strength of the chitin and chitosan is very low. The chitosan films can be prepared to investigate the mechanical properties. Mostly tensile strength and percentage elongation is measured to investigate the mechanical strength of the material. The mechanical strength of the biopolymer can be increased by preparing chitosan composites and blends. A recent study is reported on extraction methods of chitin from crab shell and investigation of its mechanical properties [20]. The present paper describes the preparation of chitin from Narmada riverside crab shells and investigation of mechanical properties of chitosan based films.

2. MATERIALS AND METHODS

2.1. Preparation of Chitin and Chitosan

The raw material used in present work was Narmada River Side Crab Shell collected from the fish markets of Nimad region of Khargone, MP, India. Crab shells were cleaned and washed thoroughly to remove any foreign materials, followed by grinding to get particle size 0.30-0.35 mm. The crab shell were collected and processed to extract chitin and chitosan. Grinding, demineralization, deproteinization etc. were the main steps followed by filtration and drying. The chitin and chitosan extracted as described by Gadagey and Dey 2017[21] with some modifications.

2.2. Preparation of Chitosan Films

Chitosan films were prepared by solution casting method. The prepared chitosan was used for film preparation. Acetic acid was used as a solvent and glycerol was used as a plasticizer. The films were prepared by the solution casting as described by Han et al. [22] with some modifications. The extracted chitosan from Narmada riverside crab shells were used to prepare the chitosan film. In a 250 ml beaker 100 ml demineralized water was used to dissolve 2gm chitosan with 2 ml acetic acid. The solution was stirred overnight with magnetic stirrer on hot plate at 40°C temperature. After complete dissolution of chitosan, glycerol was added as a plasticizer. Four moulds were prepared with 0%, 30%, 60% and 90% glycerol (w/w of chitosan). The samples are coded as CS-00, CS-30, CS-60 and CS-90 respectively. The solution was filtered through coarse sintered glass filter to remove un dissolved impurities. The solution was poured onto glass moulds. The films were dried for four days at ambient temperature. The films were peeled off and conditioned for testing.

2.3. Specimen Preparation

The peeled off films were cut into pieces to prepare specimens. The specimens were stored separately according to their compositions.

2.4. Film Thickness Measurement

Film thickness was measured using a Dial Micrometer Mitutoyo, SN. 7327P. The least count was one micron and range 0 to 1000 micron. Ten measurements were taken at random positions around the film samples and the mean values were calculated.

2.5. Tensile Testing of Chitosan Based Films

Mechanical properties were determined using a tensile test with grip separation of 50 mm and speed rate of 0.9 mm/s, according to the ASTM D882 standard method. The samples were cut into strips (20mm x 100 mm). These tests were carried out using a Tensile Testing Machine, Model Dutt 105, Ahmedabad(India).

3. RESULTS AND DISCUSSIONS

Narmada riverside crab shells processed to prepare chitosan based films. The films were tested for tensile strength and percentage elongation. Table 1 shows Tensile Strength and Elongation at Break of Chitosan based films incorporated with different Film Thickness.

Table 1 Tensile Strength and Elongation at Break of Chitosan based films incorporated with different Film Thickness

S.NO.	Sample	Film Thickness mm	Elongation at Break %	Tensile Strength MPa
1.	CS-G00	0.110	13.6	122.62
2.	CS-G30	0.126	30.8	85.03
3.	CS-G60	0.268	39.6	40.75
4.	CS-G90	0.324	45.6	32.68

3.1. Film Thickness Analysis

The thickness of the Chitosan based films ranged between 0.110 and 0.324 mm, and the values were significantly influenced by the loading concentration of plasticizer. The observations are in close agreement with Ahemed et al. 2017 [23] and Shankar et al. 2016[24]. Bhuwaneshwar et al. 2011[25] prepared chitosan films with different percentage of chitosan and acetic acid. The film with 2 g chitosan and 2% acetic acid achieved 0.170 mm. The film thickness of pure chitosan film (CS-G00) is 0.110 mm. Maximum film thickness 0.324 is observed at 90% glycerol added chitosan film. The pure chitosan film has minimum film thickness. The film thickness increases with increase in glycerol percentage. The variation of film thickness with glycerol is shown in Figure 1. There is very small increase in film thickness by adding 30% glycerol in chitosan. The film thickness significantly increases from 30% to 60% region. Again small change in thickness observed from 60% to 90% region. Thickness is very important parameter in many applications of chitosan films.

3.2. Percentage Elongation Analysis

Percentage Elongation at Break of chitosan based films were measured using Tensile Testing Machine with gauge length 50 mm. The change in length recorded and Percentage Elongation at Break calculated. It is clear from the results that the EAB increases as the glycerol percentage increased. The maximum value of EAB is 45.6% whereas minimum value is 13.6 %. Between CS-G00 and CS-G30 significant increase in EAB is observed. Between CS-G30 and CS-G90 constant change in EAB is observed. Figure 2 represents the Elongation at Break of Chitosan based films incorporated with different Film Thickness. Both EAB and FT increases with increase in glycerol content. Delavar & Shojaei 2017[26] reported pure chitosan film EAB 40%. The maximum EAB was reported by Ahmed et al. 2017[23], 72.70% which is more than present study but at this EAB value the TS was only 6.99 MPa whereas in the present study the TS is 122.62 MPa. Bhuvaneshwari et al 2011[25] achieved EAB 64% at TS 44.12 MPa. The minimum EAB 2.25% is reported by Liu et al. 2017[27] at TS 51.04 MPa.

3.3. Tensile Strength Analysis

The strength of pure chitosan films and Glycerol blended films was measured on tensile testing machine. Tensile Strength and Elongation at Break of Chitosan based films incorporated with different Film Thickness is shown in Table 2. Maximum TS was recorded for pure chitosan films with TS value 122.62 MPa at EAB 13.6% and FT 0.110 mm. Between CS-G00 and CS-G30 significant reduction in TS is recorded. Between CS-G30 and CS-G60 nominal change in TS is observed whereas between CS-G60 and CS-G90 small reduction in TS is observed. The TS continuously decreases with increase in glycerol. The present study achieved TS 122.63 MPa at EAB 13.6%.. The value of Tensile Strength depends on the chitosan quality. The degree of deacetylation of chitosan also affects the value of Tensile Strength of the film. In the present study Narmada Riverside Crab shells are used to prepare

the chitosan. The prepared chitosan is represented quality results. Khan et al 2000[28] achieved TS 67.11 MPa at EAB 21%.The previous research results reported TS value ranged 6.99 MPa to 98.26 MPa. Hence the present study achieved good results. Fundo et al.201 [29] worked on chitosan- glycerol films. They reported TS 0.281 MPa, EAB 32.67% incorporated with 90% glycerol films. Figure 1, 2 &3 represents the FT, EAB and TS analysis.

Figure 1 Film Thickness of Chitosan based films incorporated with different percentage of Glycerol

Figure 2 Elongation at Break of Chitosan based films incorporated with different Film Thickness.

Figure 3 Tensile Strength and Elongation at Break of Chitosan based films incorporated with different percentage of Glycerol

The mechanical characterization of chitosan based films has been done by many researchers[31]. The pure chitosan films have been characterized. Table 2 represents the various Thickness, TS, and EAB values of pure chitosan films reported earlier.

Table 2 FT, TS, and EAB values of pure chitosan films reported earlier.

S.NO.	Reference	Code	FT mm	TS MPa	EAB %
1.	Ahmed et al. 2017[23]	AH17	0.172	6.99	72.70
2.	Bhuvaneshwari et al. 2011[25]	BH11	0.170	44.12	64.00
3.	Bujang et al. 2013[32]	BU13	0.175	26.12	25.00
4.	Chen et al. 2016[30]	CH16	0.026	98.26	04.16
5.	Liu et al. 2017[27]	LI17	0.031	51.04	02.25
6.	Present Work	CS-G00	0.110	122.62	13.6

The FT of various previous results for pure chitosan films ranged 0.026 mm-0.175mm. The present work FT is 0.110. The film thickness of pure chitosan is depends on the preparation of solution. The chitosan should be completely dissolved in acetic acid solution. The film forming duration and drying condition also affect the FT. The EAB of previous results for pure chitosan films ranged 02.25% - 72.70%. The present work EAB is 13.6%. The greater values of EAB of previous researches are associated with very small values of TS. The present EAB 13.6% is associated with TS 122.62 MPa. Hence the EAB in the present work is justified. The TS of previous results for pure chitosan films ranged 6.99 MPa- 98.26 MPa Chen et al. 2016[30] achieved TS 98.26 MPa which is good result but EAB is very low (04.16%). Liu et al. 2017[27] also achieved TS 51.04 MPa but again the EAB is extremely low (02.25%). Bujang et al. 2013[32] achieved TS 26.12 MPa associated with EAB 25.00% and FT 0.175.

4. CONCLUSIONS

Mechanical property is important for chitosan films because adequate mechanical strength can ensure film's integrity and protect film from minor defects. Tensile strength and elongation at break are two key indexes reflecting the mechanical property of film. Tensile strength is the maximum strength for a film withstanding against applied tensile stress, and elongation at break represents the ability of a film to stretch. The investigation of the mechanical properties of chitosan films are required to understand the mechanical behavior of the chitin prepared from Narmada Riverside Crab Shells. Tensile strength and Percentage Elongation at Break of the films determine their performance and integrity during storage, utilization and handling. Samples were tested for tensile strength and Percentage Elongation at Break. There is a optimum point with TS 85 MPa and EAB 30.8%. This optimum value is represented on CS-G30 film. . The present work TS is 122.62 MPa that suggests the researchers to use the Narmada Riverside Crab Shells for the chitosan production.

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