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Mechanical and Barrier Properties of Biodegradable Films Made from Chitosan and Natural Fiber Blends

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ABSTRACT

In the present work, biodegradable film blends of chitosan with fibers were used to prepare by mixing solution and film casting. Film blends were also prepared by increasing the weight ratio of chitosan. The main aim of these blends is to improve the mechanical properties of chitosan by blending with biodegradable natural fibers. Mechanical properties of the obtained film blends were assessed by tensile modulus. Swelling test, scanning electronic microscopy and biodegradability studies were used to analyze the influence of the incorporation of fibers in the film properties. The incorporation of fibers to chitosan tensile modulus of the films decreased but 2.5grams chitosan is showing good result compared to 3grams chitosan. However, Water absorption properties and biodegradability of films were also decreased. Scanning electronic microscopy showing good results. Mechanical properties revealed that chitosan and fiber blends are inconsistent.

Keywords: B-Banana, Biodegradable films, Blends, Chitosan, C-Coir, M-Mercerization, Samples.

1. INTRODUCTION

Environmental deterioration is directly the outcome of pollution of soil, air and water. The extend of industrialization and agriculture has been significantly responsible for extremely toxic chemicals entering into the natural streams through industrial and municipal effluents. Prevention and control of pollution is therefore, a necessity. It is very important to bring about reconciliation between development and conservation of environment and ecology. The concept that food supply must nutritionally be adequate, equitable shared, socially affordable and predictable leads to intensive agricultural practices for enhanced food production, better storage and preservation and diversified processing and packing methods. The packaging supplies including food stuffs are far more different and complex than those of other non-food products. The main functions of a packaging material are to protect, present, and dispense the products.

Packaging is important in post-harvest upkeep of fruits, vegetables, and processed ingredients for confident shelf life extension. The raw substances of food, in addition to the innumerable quantity of processed foodstuffs made available inside the market are extraordinarily perishable and want effective and efficient packaging systems for extending their shelf existence and availability, specifically in distant places[1][2]. safety of foodstuffs pertains to the price of exceptional exchange, which include each physical (mechanical damage at some stage in transit or garage, lack of consistency or crispiness, loss of appearance, and sales appeal) and organoleptic (lack of flavor, color, and smell) modifications. Thus, the package deals have to guard the food product in opposition to physical hazards and atmospheric/environmental factors inclusive of water vapor, gases, and odors. Through a suitable combination of structural design and material selection, food packaging

should ensure conducive surroundings internal and hold the food products through keeping greatest inner gaseous ecosystem; packaging need to also be effective in opposition to outside deteriorative influences [3].

Sadly, there are some boundaries to the application of chitosan film for packaging, because of its high sensitivity to moisture. One approach to overcome this drawback is to relate chitosan with a moisture resistant polymer, whereas maintaining the overall biodegradability of the product. Involvement between polymers can be blends or multilayer products, for example, coatings or laminating, but blending is easier and more successful technique to prepare multiphase polymeric materials with desirable properties [4].

The aim of this study is to improve the mechanical properties of chitosan by blending it with natural fibers and to obtain biodegradable films blends that are completely degradable. In this work, blends of chitosan and fibers have been prepared by the solution mixing and film casting. Different chitosan/fibers ratios were tested. However, chitosan should remain the major phase in the blends to keep a potential to be an antimicrobial film. Mechanical properties were evaluated. The miscibility of a chitosan/ fiber blend was discussed by analyzing the change of the mechanical properties of blends as a function of the blend ratio.

2. MATERIALS AND METHODS

2.1 Materials

The chitosan used was a marketable material brought from shrimp shell (blueline foods pvt ltd., India). Chitosan is the N-deacetylated derivative of chitin (by treatment with hot alkali), its structure is composed of 2-amino-2-deoxy-β-D-glucose (D- glucosamine) in a β(1-4) linkage, and with occasional N-acetyl glucose- amine residues. The structure of chitin and chitosan resembles cellulose except at position C-2, being replaced by acetamido and/or amino groups [5].

Chitin is exceedingly insoluble, of low chemical reactivity, tough, white inelastic, nitrogenous polysaccharide [6]. A critical parameter, which influences its physical chemical and biomedical characteristics, is the diploma of N-acetylation mainly, in chitosan that is the ratio of two-acetamido-2-deoxy-D-glucopyranose to 2-amino-2-deoxy-D -glucopyranose structural devices. This ratio has a hanging impact on its solubility and solution houses. Chitin is N-deacetylated to such a quantity that it (chitosan) turns into soluble in dilute aqueous acetic acid and formic acid. Converting chitin into chitosan lowers the molecular weight, adjustments the diploma of N-acetylation, and thereby alters the net rate distribution, which in flip impacts the degree of agglomeration. The weight –average molecular weight of chitin is 1.03 to 2.5 x 10^6, but upon N-deacetylation it reduces to 1.0 to 5 x10^5 [7].

The banana and coir fibers brought from go green products which are in long form are cute into short fibers. With a global shift towards green economy, these natural fibers are being currently explored as viable components for the fabrication of biocomposites in combination with thermoplastic and thermosetting polymers, on account of their natural abundance, light weight, low cost, renewability, biocompatibility, biodegradability and thermal insulation properties [8-12]. Among the many types of natural fibers, flax, jute, hemp, rice straw, banana, sisal, cotton, coir, bamboo, kenaf, ramie, kapok and pineapple fibers are being actively used as bio-

sorbents and components in bio-based composites [13]. Natural fiber composites are seen as potential reinforcements in polymeric matrices due to their inherent mechanical strength and non-toxicity [14].

Banana fiber reinforcement significantly enhanced the mechanical performance of epoxy/glass composites [15]. Short banana fiber -reinforced natural rubber composites prepared by vulcanization technique exhibited enhanced thermal and dimensional properties [16]. Alkali treatment of banana fibers positively influenced the tensile strength of the composites, as was reported for a banana fiber- soy protein green composite [17]. The results indicated that coir can be used as a reinforcing material for making low load-bearing thermoplastic composites [18] [19] .Used 50% NaOH on coconut fibers whereas5% NaOH was found to be sufficient for the effective mercerization of oil palm fibers [20] and coir fibers [21].

Adhesion between natural fibers & polymers and the mechanical properties of the blends have been reported to be enhanced by employing surface pre-treatment of fibers by chemical modifications through alkali treatment (mercerization), acetylation, silane treatment, graft copolymerization, etc.,[22-24]. Chemical treatments such as acetylation, benzoylation, methylation, cyanoethylation and acrylation lead to decreased surface hydrophilicity of the fibers [20, 25]. Among all chemical treatments, mercerization is one of the well known alkali treatments to remove lignin, pectin and other waxy materials present in the fiber covering the external surface of the fiber cell wall. Mercerization generally decreases the hydrophilicity and increases the accessibility to hydroxyl groups of the fibers, thus providing better bonding sites on the surface [26].

The solvents were acetic Acid from chemical house. This is selected due to it shows best results and good to peel from the casting plate [3].

2.2 Sample Preparation

Blends of chitosan with natural fibers were prepared with some modification of the methods of Olabarrieta et al. [27]. Mercerized fiber was soaked in 2% acetic acid solution for 1 day. Chitosan was separately dissolved in 2% acetic acid solution and slowly added to the fiber and stirred for 1 day. Then it was cast in a Petri dish plate and kept it for vaporization process of 36 hr allowed to dry. The final compositions (chitosan/fibers) were designated 2.5C, 2.5C1MB, 2.5C1MC, 3C, 3C1MB and 3C1MC. [1]

3. Experimentation

3.1 Tensile Modulus

The mechanical properties (tensile modulus) of the prepared films (average of films) were determined at 25°C using Universal Testing Machine (UTM) possessing a load cell of 5 KN with displacement rate of 2 mm/min. at room temperature. The gauge length and width of all specimens were 50 mm and 15 mm respectively (ASTM D 638).

3.2 Swelling Test

Swelling test is a widely followed method to obtain water absorptive of polymeric samples. Though unsophisticated, it is simple toper form and generally yields good, reproducible results. The water absorption

studies were carried out for all the films and calculated for each film through swelling test. The pre weighed (dry weight) films were immersed in the water. After a period of 1hours, samples were removed and the weight of swollen samples was recorded (wet weight). The extent of water absorption was calculated as follows:

Extent of water absorption = (Difference in weight x 100) / Initial weight.

3.3 Scanning Electron Microscopy (SEM)

The surface morphology and cross section morphology of the composites were observed with scanning electron microscope to verify the compatibility of the mixtures of chitosan with fibers. For the analysis the composites were cut into pieces of various sizes and wiped with a thin gold - palladium layer by as putter coater unit.

3.4 Biodegradable Test

Biodegradation is a form of progression of activities at some stage in which substances are dissolved chemically through bacteria or some other biological ways. Maximum biodegradable count includes organic substances generated from plant life, animals or artificial materials which can be comparable sufficient to plant and animal be counted. Here is the use of PBS solution for biodegradable test. Phosphate buffered saline (PBS) is a buffer solution commonly used in organic research. The buffer allows maintaining a constant PH. Normally a pH of 7 is maintained. The ion concentrations of the solution usually match those of the human body.

Once the solution is prepared, weigh out the specimen and make a note of it in table, after 24 hours, take away the specimen from solution and wash with distilled water and dry it completely. Weigh the specimen again and carry on the procedure. By weighing the initial and final weight of the specimen we can calculate the loss of weight of the specimen by using the formula.

Weight loss = initial weight – final weight.

4. RESULTS AND DISCUSSION

4.1TensileModulus

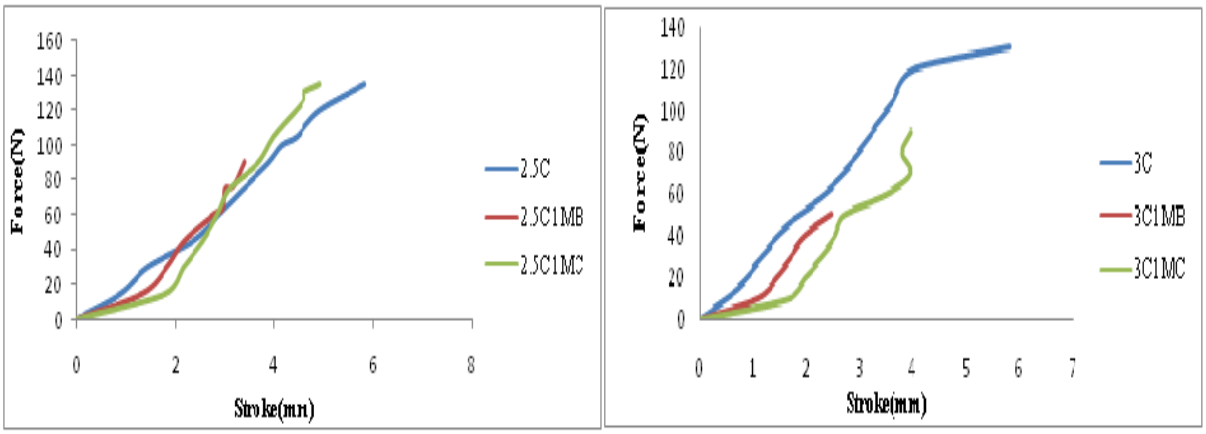

Figure 4.1: Force vs stroke for all chitosan films

Table 1: For tensile modulus

Films	Maximum Force (N)	Maximum Displacement (mm)	Maximum stress (N/mm^2)	Maximum strain (%)	Modulus (N/mm^2)
2.5C	118.33	3.877	34.871	9.19	783.845
2.5C1MB	76.33	3.293	5.4831	6.589	172.789
2.5C1MC	130.66	4.764	38.136	9.65	287.830
3C	112.22	4.285	32.535	8.7	730.449
3C1MB	42.33	2.066	3.013	4.23	135.045
3C1MC	84.424	3.351	7.924	8.70	215.28

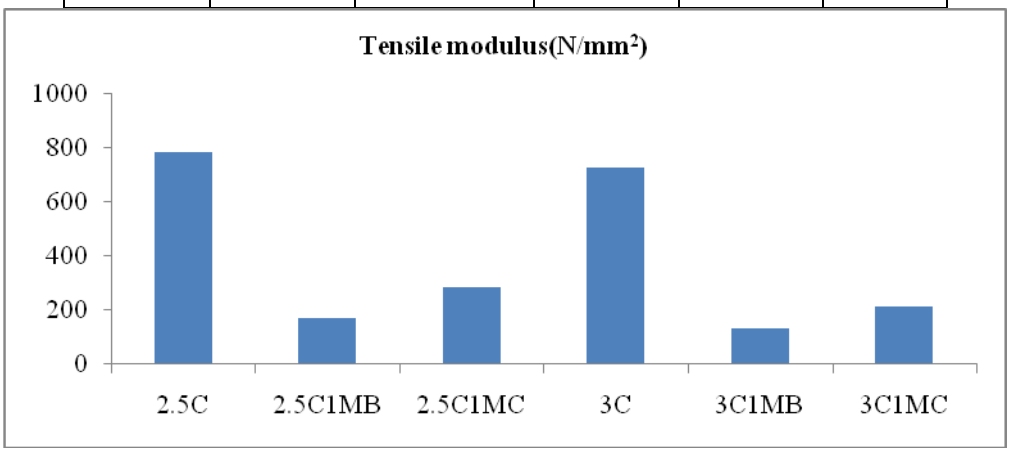

Figure 4.2: Graph for tensile modulus

From the graphs above shows the sample tests tensile modulus with a different weight ratio and by adding fibers. Table 1 shows maximum force, maximum displaysment, maximum stress, maximum strain and tensile modulus of all samples. Tensile modulus is important to measure the stiffness of sample with different weight ratio chitosan with fibers. Sample with 2.5g chitosan shows the higher value of tensile modulus followed 3g chitosan. The resulted were analyzed by the increase value of tensile modulus with the increase weight ratio of chitosan. The lowest tensile modulus is the sample with 3C1MBchitosan. In both 2.5C1MB and 3C1MB are showing less tensile modulus compare to coir fiber films. So that by adding banana fibers to the chitosan it decreases modulus of film. Moreover, the 2.5C1MC and 3C1MC are better compared to the banana fibers. 2.5C film is showing best compared to the all other films. The resulted were analyzed increase value of tensile modulus with the less weight ratio of chitosan that is without fibers. But the different is the by adding the fibers, 2.5C1MC film produce the higher tensile modulus value compared 3C1MC and banana fiber films.

Polysaccharides usually have a strong affinity for water because of the presence of significant amount of hydrophilic groups. As films, they can be easily hydrated. In order to evaluate a potential application, swelling experiments are necessary to analyze the film stability during the swelling process because of the exudates produced during the healing process.

4.2 Swelling Test

Figure 4.3: Films after taken out of test

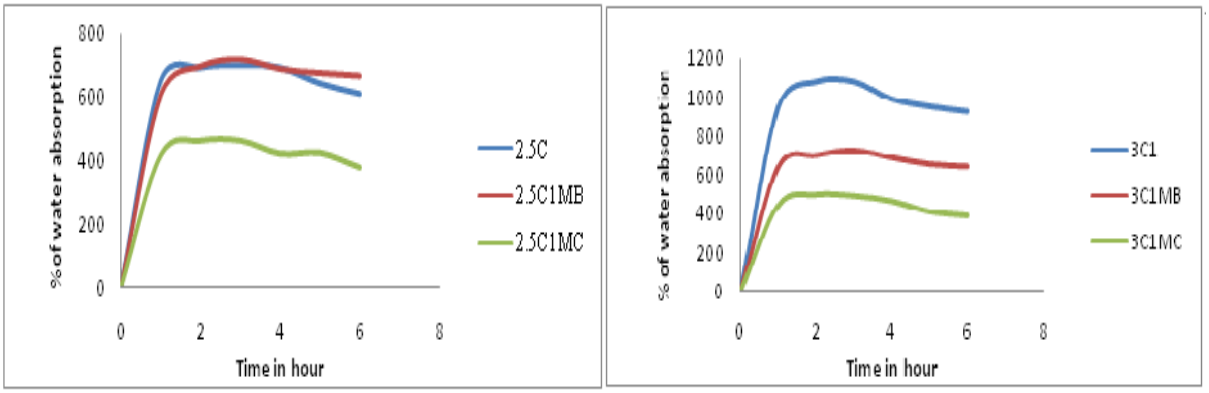

Figure 4.4: % of water absorption vs time in hours for all chitosan films

The hydration properties of polysaccharides depend on primary and supra macromolecular structure which are influenced by the presence of fibers. As shown in Fig 4.4, the swelling degree of chitosan films was affected by the different fibers. The film prepared without fibers could not reach an equilibrium swelling degree and after some time in contact with water, the film broke apart as shown in Fig 4.3. Films obtained from the fibers displayed a higher equilibrium swelling degree. The amount of absorbed water by the films initially it was more up to 3hr and after that they vomited water and its weight was reduced. The introduction of amounts of fibers favored the dimensional stability of the films. This behavior could be associated to the establishment of the cross-linked network induced by hydrogen intermolecular bonds between chitosan and fibers. These interactions were responsible for the limited swelling behavior compared to the films prepared.

4.3 SEM

4.3.1Morphological Study of Chitosan

The surface morphology of Chitosan film is appeared in Fig 4.5 (a) indicated even morphology of the film and the total scattering of chitosan particles. It was clear that the film was permeable and numerous voids were available in the surface of the film. It was seen from Fig 4.5(b) that the surface of the filaments indicated miniaturized scale fibrillation which was accomplished through mercerization. Demonstrated the smooth morphology of the fiber in the film.

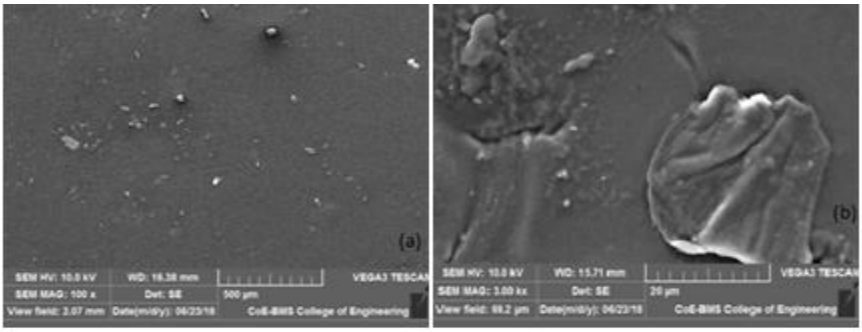

Figure 4.5: (a) and (b) SEM images of Chitosan film

4.3.2 Morphological Study of Chitosan banana Fiber

The SEM pictures of Chitosan banana fiber are given in Fig 4.6 (a) demonstrated the arbitrary plan of filaments and the nearness of less voids at first glance. The small strands in Fig 4.6 (b) affirmed the expansion of chitosan demonstrates the best minimized capacity between them. The stacked game plan of strands and extensive thickness of the film. . It was watched that unit of fiber from grid was less in chitosan-mercerized banana fiber films. SEM may have shown of extensive interfacial bond amongst chitosan and banana fiber.

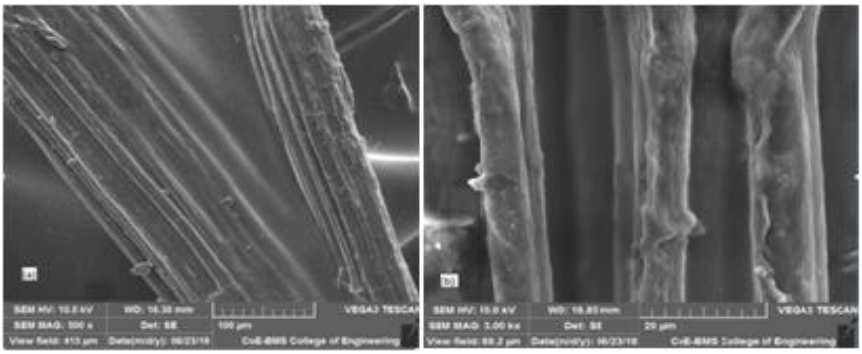

Figure 4.6: (a) and (b). SEM images of Chitosan-banana film

4.3.3 Morphological Study of Chitosan coconut Fiber.

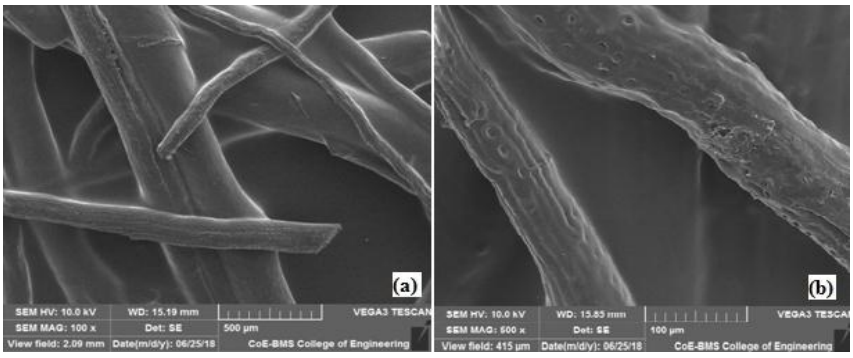

Figure 4.7: (a) and (b) SEM images of Chitosan-coconut film

The SEM pictures of Chitosan coconut fiber are given in Fig 4.7 (a) demonstrated the arbitrary plan of filaments and the nearness of less voids at first glance. The small strands in Fig 4.7 (b) affirmed the expansion of chitosan demonstrates the best minimized capacity between them and observed some pores on the fiber covered with chitosan. The stacked game plan of strands and extensive thickness of the film. It was watched that unit of fiber

from grid was less in chitosan-mercerized coconut fiber films. SEM may have shown of extensive interfacial bond amongst chitosan and coconut fiber.

4.4 Biodegradation test

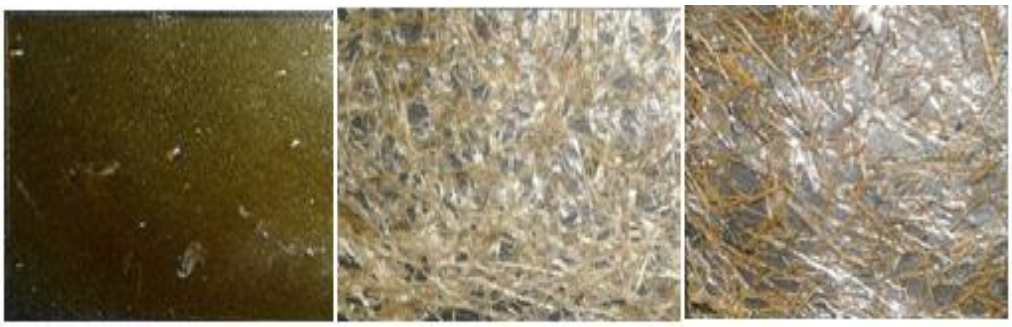

Figure 4.8: Neat films before the test

Figure 4.9: Films after 4 days

Figure 4.10: Films after 8 days

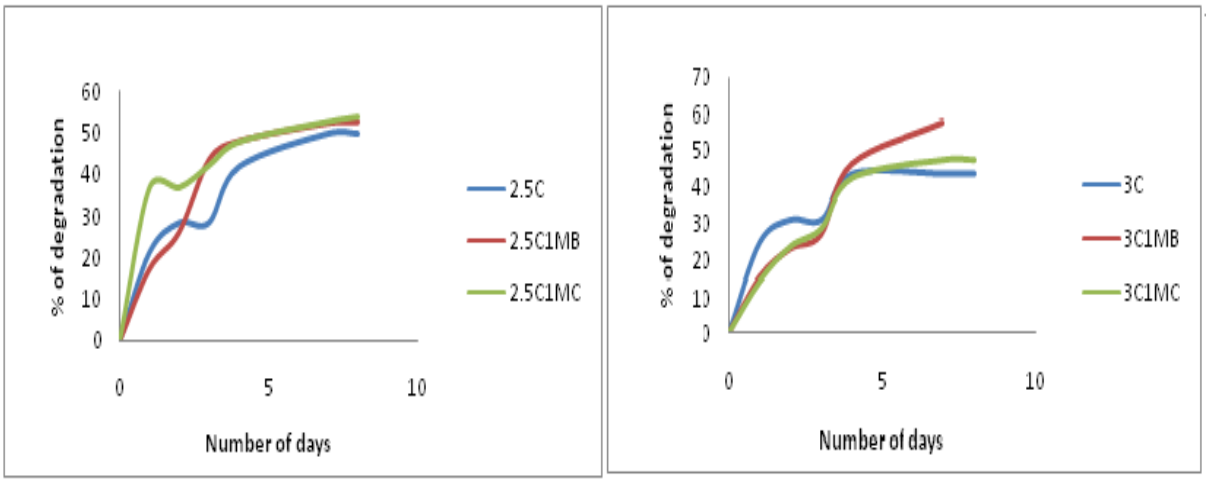

Figure 4.11: % of degradation vs number of day's for all chitoson films

One advantage of films prepared with biodegradable materials is related to the reduction of environmental pollution. The physical changes in surface morphology of films were qualitatively studied. Fig 4.8 presents a film of neat films before the test and Fig 4.9, 4.10 shows the changes produced on the surfaces of films after 1 to 8 days in contact with chemical solution. A progressive change on the surface of samples including cracks, holes, color changes and microorganisms appearance was visually observed. Films without fiber were completely degraded after 20days. The films prepared fibers were chitosan was completely dissolved in solution and fibers were remaining.

Fig 4.11, shows the variations in the films after 1day for films prepared with the amount of fibers. The same trend was observed for all the samples.

5. CONCLUSION

Chitosan is a promising biodegradable polymer for active food packaging. However, because of its sensitivity to moisture, in this work it has blended with natural fibers, thus obtaining biodegradable film blends that are completely from renewable resources. The mechanical properties of chitosan/natural fiber blend reveal that a phase separation in the blend has occurred, indicating their incompatility. The mechanical characteristics of the blends decrease in the fiber contents. Moreover, water absorption properties show that as fiber are add, water absorption film decrease as compared to the chitosan film. In spite of their incompatibility, the incorporation of fibers could improve the water absorption properties of chitosan. SEM may have shown of extensive interfacial bond amongst chitosan and fibers. Biodegradation of chitosan film faster compared to blend natural fiber films they may more days to degrade as we know fibers are degradable.

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