Biodegradable Plastic Based on Cotton linter: Preparation and Characterization

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Abstract

Biodegradable plastic produced from vital natural materials to be the best solution for treating the pollution caused by the traditional plastic, the chemical cross linkers are often used to improve the mechanical properties. The aim of this paper is to produce the biodegradable plastic by extracting cellulose from cotton linters. The biodegradable plastic prepared by extracted cellulose from cotton using acetic acid and some other chemicals at low temperature. Two types were used polyethylene glycol and Sudanese gum Arabic as plasticizer and compared the terms of product and decomposition. The effects of crosslinking between cotton linter with plasticizer blend on physical, mechanical and biological properties were investigated. The morphological characterization were evaluated by S.E.M and FT-IR , and compared with pure cellulose. The obtained results indicate that when a natural plasticizerwas added to cellulose the internal structure of the materials changes. On the contrary, samples with the highest content of natural plasticizer (15%) showed the less regular structure and the highest total porosity. The effects of acids, alkalis, salts on cellulose acetate of the biodegradable plastic decompose in a compost bin for 2 weeks were investigated. The addition of Sudanese gum Arabic as important factor related to the product properties, it seems that the biodegradable plastics were doing really good comparing with the conventional plastic.This information about the biodegradable plastics can become very useful in the future because could be be environmentally friendly. Currently the

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biodegradable plastics are not cheap and recyclable; however it reduces the greenhouse gases.

Keywords: Biodegradable plastic, Crosslinkers. Cotton linter, Plasticizer.

المستخلص

البلاستيك القابل للتحلل الحيوي المنتج من مواد طبيعية حيوية هو أفضل حل لمعالجة التلوث الناجم عن البلاستيك التقليدي، يتم استخدام المواد الكيميائية المتشابكة في كثير من الأحيان لتحسين الخواص الميكانيكية. الهدف من هذه الورقة هو إنتاج البلاستيك القابل للتحلل عن طريق استخراج السليلوز من شعيرات القطن. يتم تحضير البلاستيك القابل للتحلل بواسطة السليلوز المستخرج من القطن باستخدام حمض الأسيتيك وبعض المواد الكيميائية الأخرى عند درجة حرارة منخفضة. تم استخدام مادتي البولي إيثيلينجلايكول والصمغ العربي السوداني كملدن ومقارنة شروط المنتج والتحلل. تمت دراسة تأثير التشابك بين شعيرات القطن مع الملدنات على الخواص الفيزيائية والميكانيكية والبيولوجية. تم تقييم توصيف المورفولوجية باستخدام جهازي (SEM, FT-IR) ومقارنتها مع السليلوز النقي.

تشير النتائج التي تم الحصول عليها إلى أنه عند إضافة الملدنات الطبيعية إلى السليلوز، يتغير الهيكل الداخلي للمواد. على العكس من ذلك، أظهرت العينات ذات المحتوى العالي من الملدنات الطبيعية (15٪) البنية الأقل انتظامًا وأعلى مسامية كلية.تم التحقق في آثارالأحماض والقلويات والأملاح على أسيتاتالسليولوز من البلاستيك القابل للتحلل الحيوي لمدة أسبوعين. إن إضافة الصمغ العربي السوداني كعامل مهم متعلق بخصائص المنتج، أشارت الي أن اللدائن القابلة للتحلل الحيوي كانت جيدة مقارنة بالبلاستيك التقليدي. يمكن أن

تصبح هذه المعلومات عن اللدائن القابلة للتحلل البيولوجي مفيدة للغاية في المستقبل لأنها يمكن أن تكون صديقة للبيئة. إن المواد البلاستيكية القابلة للتحلل حالياً ليست رخيصة ويمكن إعادة تدويرها ؛ ومع ذلك فإنها تقلل من غازات الاحتباس الحراري.

1. Introduction:

Today consumer driven society demands plastic for the manufacture of millions of products. Packaging materials largely contribute to the high demand for plastics. Our fast paced lifestyles demand convenience and single serving, pre-packaged foods. The manufacture of cost effective packaging that adequately protects the product is made possible by plastic. Plastic is made from crude oil, anon renewable resource. Although the plastic we use can be recycled, the amount of solid waste generated by plastic is becoming a problem. In recent years, natural renewable resources have successfully been used to produce plastic that is biodegradable under certain temperature and humidity conditions. Biodegradable plastic made from renewable resources is an important material innovation because it decreases dependence on petroleum and reduces the amount of waste material, while still yielding a product that provides similar benefits of traditional plastics. [1]

Over the last fifty years, the production of plastic has reached enormous levels. Approximately two hundred billion pounds of plastic are produced worldwide every year. This equates to about forty pounds of plastic per person, per year. Between thirty and forty-two percent of plastic produced is used for packaging. Of the plastic produced, more than sixty billion tons are thrown away every year in the United States. Approximately half of this waste is attributed to packaging.

The oil that is used as a raw material, as well as the oil required for energy, consumes between six and eight percent ofthe total world oil production. Although this is a small percentage, over time the amount of petroleum used to make plastic does contribute to the depletion of fossil fuels. The rate of consumption influences the overall price of petroleum, contributing to the current rise in raw material costs.Plastics derived from petroleum are made from synthetic polymers. In 2002, the production of biodegradable plastics was less thanone percent of the production of plastics. One of the more commercially successful plastics is PLA, so named because it is produced from the poly lactic acid found in corn, present in the metabolism of all animals and microorganisms and does not produce toxic byproducts when it biodegrades. A leader in the packaging arena, PLA is currently only produced on a small commercial scale, most closely resembles polyethylene in structure and properties, a hard, transparent and crystalline plastic. The resin is also clear, stiff, glossy and has flavor and aroma barrier properties similar to PET. Another example is microbial Poly-HydroxyAlkanoates (PHA) which for the past many years has been developed as biodegradable plastics. PHA has been marketed as environmentally friendly bio-plastics with less CO_2 emissions and sustainability as well as independence from petroleum sources. Also, there were studies of their industrial applications. [2]

In recent years the development of biodegradable packaging materials from renewable natural resources (e.g. crops) has received increasing attention, particularly in EU countries and the use of renewable resources has been revitalized.If properly managed, this would reduce their environmental impact upon disposal and also, it would be technically and economically practicable. Biodegradable plasticsbased on cellulose acetate (CA) were studied and the

produced plastic decomposed in soil or water within a few years. However, the material can be recycled also, or incinerated without residue. There were studies of the important properties of CA including mechanical strength, impact resistance, transparency, color ability, fabricating versatility, mold ability and dielectric strength, CA could be used for the manufacturing of photographic films, ultra - filtration membranes, fibers and some plastic tools. Natural plastic is produced in a fluid form and therefore, it is shaped easily and does not require a large amount of energy. This is to be compared with the conventional plastic which is stored usually as granules and needs a massive amount of energy so that it can be shaped by molding, injection, or extrusion. [3]

In Sudan now the government has begun enacting laws banning the use of traditional plastics. In 2009 an environmental protection conference was recommended to prevent the use of traditional plastics and face the research for alternatives to it. One of the proposed alternatives was the use of environmentally friendly plastics, namely bio- plastic. [4]

1.2 Advantages of Bioplastics:

They were produced from renewable raw materials, have a relatively long, stability depending on their composition, can be degraded biologically, can be decomposed into non-toxic source materials and were CO_2-neutral. Economic used can be made of overcapacities in agriculture, which also makes ecological sense.Figure (1.1) shows the overview Bio-Plastic.[1]

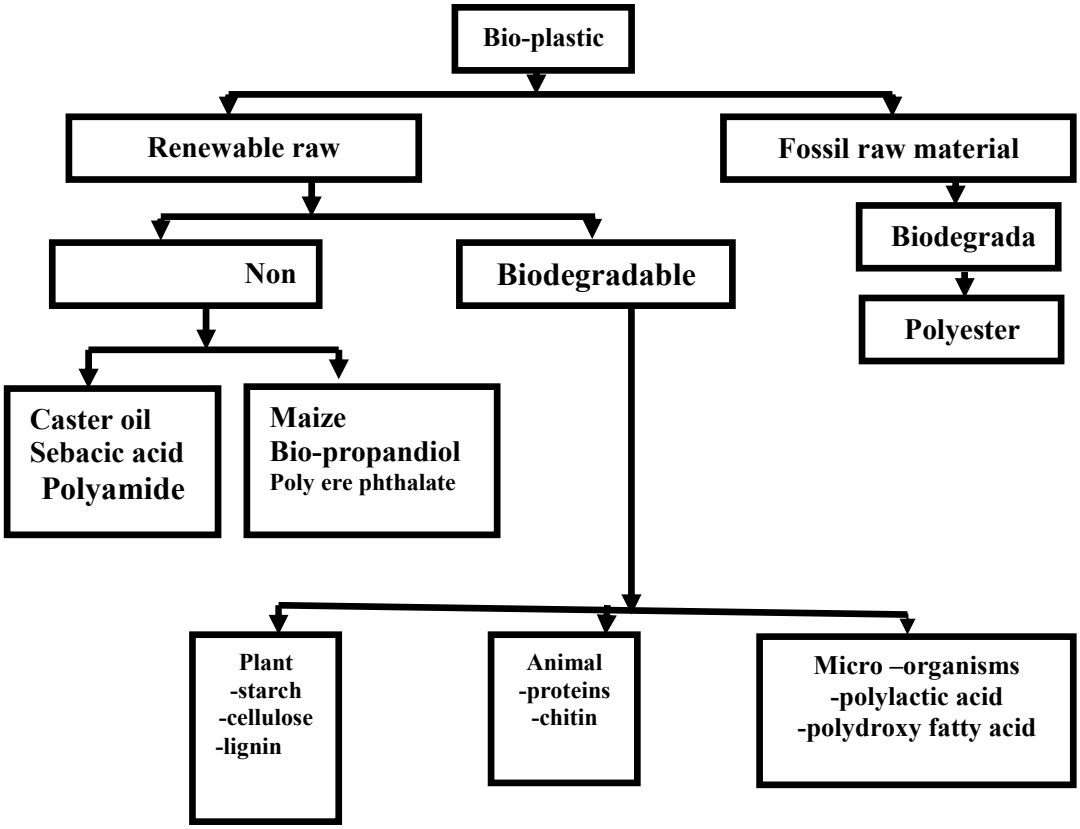

Figure (1.1): Overview the Bio-Plastic.

Mostafa etal.reports an efficient method for the production of the cellulose acetate bio-fiber from flax fibers and cotton linters. The used process satisfied a yield of 81% and 4% for flax fibers and cotton linters respectively (based on the weight of the cellulosic residue used). [5]Ioannaetal.were wrote a paper biodegradation of agricultural plastic films. [6]Martinet al.prepared the polyhydroxyalkanoatesfrom agricultural waste and surplus materials. [7]Biochemical, mechanical, and spectroscopic analyses of genetically engineered flax fibers producing bio-plastic (Poly-b-Hydroxybutyrate)Magdalenaet

al. [8]Richard Chen, prepared new engineered materials from biobased plastics and Lignin.[9]

In this article, a new approach was introduced to prepare the biodegradable plastics from natural materials such as cellulosecotton.The influence on the contents and dispersed condition of additives in cellulose cotton matrixes on the biodegradable plastics mechanical strength were investigated in order to obtain applicable biodegradable plastics. The morphology and structures of polymer network was also observed by some experimental analysis techniques, such as scanning electronic microscope (SEM).

2. Experimental and Methods:

2.1 Materials and Chemicals:

Cotton linters were purchased from (Gazira Cotton). Glacial acetic acid, acetic anhydride, sulfuric acid were used as a catalyst and for the acid resistance test; polyethyleneglycol 600was used as a plasticizer. Acetone (was used as a solvent).Sodium hydroxide, lead acetate, ferrous sulfate and tri- sodium orthophosphate(from lab link company) were used for testing acids, alkalis and salts to the produced CA's resistance. Gum Arabic (was used as a plasticizer).

2.2 Procedures of Manufacturing from Cotton:

Colors and dusts were removed from cotton linters by washing with water and bleaching with 120 ml of household bleaching agent (5% NaClO&5%NaOH), thoroughly washing and then was followed by drying. A sample of 50 g of cotton linter was used. Acetic anhydride (100 ml), glacial acetic acid (100 ml) and sulfuric acid (10 ml) were mixed.The mixture was cooled to 7°C. Cotton linters were added slowly to the previous mixture with agitation to bring about the acetylating process;this step produced the primary CA. Hydration of the primary CA (viscous fluid) was achieved by diluting with 30

ml of equal parts of concentrated acetic acid (99.8%) and sulfuric acid (98%). The primary CA was allowed to age for 15 h. The resulting viscous fluid was centrifuged in order to separate the final product. Plasticizer (polyethylene glycol 600) was added as 25% by volume of the viscous CA with agitation; this formed the final product,Figure (2.1) shows that. Repeated the step above by using hashab Sudanese gum Arabic (powder) as plasticizer, was added as 25% by weight to the viscous CA to produce the final product,Figure (2.2) shows that. The product was dried natural draft tray dryer at 60°C until a constant weight in order to get the product ready for use.Before being shaped, the product was diluted with acetone to bring it into the form of a viscous fluid which could be poured in a mold or on a smooth surface for shaping.

Figure (2.1): The Final Product by using Cellulose Cotton and Polyethylene Glycol 600.

Figure (2.2): The Final Product by using Cellulose Cotton and HashabSudanese Gum Arabic.

2.3Morphological Characterization:

For morphological characterization, biodegradable plasticwas dried natural draft tray dryer at 60°C. Transverse sections were cut from dried film samples using a cold knife. Samples were then examined by a scanning electron microscope (SEM JSM-6360LV, a voltage of 20 KV, China). The working face of the samples was sprayed with gold in advance. The observed morphologies for each SEM fractograph were analyzed using Sigma Scan Pro software. Quantitative analysis of the pore size was obtained from structural indices measured from samples.

2.4Infrared Spectroscopy Testing (IR):

Absorption spectra were measured at room temperature in the spectral range using an FT-IR spectrometerandthemid IR region.

2.5Mechanical Properties:

The samples were cut into a slice shape with a thickness of 3 mm and their mechanical properties, including tensile strength at break were determined. The mechanical properties were measured at temperature of 17°C and humidity of 60%, at a crosshead speed of 50.000 (mm/min) using Instron tester - 4466, type: 42/43/4400. The elastic moduli of the biodegradable plasticwere determined by performing constant strain-rate compression measurements on an Instron 4466 mechanical tester at room temperature. The polymer sample, 15 mm in diameter and 10 mm in height, was tested at a rate of 5.000 (pts./sec's) and humidity of 40%, at a crosshead speed of 1.5000 mm/min. The results are expressed as mean value ± standard deviation with the confidence level of 95%.

2.6The Effect of Acids:

Samples (10 g) of the produced CA from cotton linters weighed precisely andput into sulfuric acid with concentrations of (10, 20 and 30)%. The samples were dried and weighed periodically for 4 days in order to determine the percentage of weight loss after each time period.

2.7TheEffect of alkalis:

Samples (10 g) of the produced CAfrom cotton linters was weighed precisely and, then, put into alkali solution (sodium hydroxide) with different concentrations (10, 20, 30 and 40)%.

2.8The Effect of Salts:

The CA produced from cotton linters was mixed with solid salt and left for 5 day, with periodic weighing every day.The objective of determining its resistance to the action of salts. The salts of ferrous sulfate, sodium chloride ,tri sodium orthophosphate and lead acetatewere used. Samples of CA weighing 10 g were used and every day the CA was removed from the salt.Thoroughly washed, dried and weighed.

2.9Breathing Test for Aerobic Organism:

The sample of 10 g is placed in container with soil and microorganism and the mixture wasventilated to provide oxygen. The microorganisms gradually digest the sampleproducing carbon dioxide (CO_2).

3. Results and Discussions

The experimental results showed that the yield of cellulose acetate was 85% from cotton linters.Thestudy used two types of plasticizer, polyethylene glycol and Hashab Sudanese Gum Arabic.The slights were difference in final product color,but it was quite irregular in terms of structures and properties. The biodegradation had shown very noticeable results for the final products from cotton linters, difference products producing by polyethylene glycol and Sudanese Gum Arabic. The product use by Hashab Sudanese Gum Arabic as

decomposing was more fluent and faster than product that used polyethylene glycol 600.

3.1Morphological Characterization:

The structures of the products cotton linter was determined by SEM. The densities of the crosslinkedpolymer containing cellulose contents from (0, 5, 10 and 15) %wtwas investigated by density measurement, SEM. The density of the crosslinked was found to increase monotonously with increasing cellulose content. Figure (3.1) showed the scanning electron micrographs of transversal sections of the films. The micrographs showed that increasing the concentration of cellulose results in higher network arrangement, what lead to porous structure on the surface of crosslinkedpolymer. The internal porosity of samples shows significant correlation between the different densitiesofcellulose contents, chemical structure of additive,the pores size and arrangement. Before adding the Sudanese Gum Arabic blends as modifying agent to cellulose blend, the cellulose polymer produced smooth structured films and exhibits a few irregular pores and the morphology is not significantly changed Figure (3.1, 0 % wt cellulose). As illustrated in Figure [3.1, (5, 10, and 15)% wt cellulose],crosslinkedpolymerwasshown highly irregular porous structure with the large pores size in 3 μm, as a consequence of the preparation technique. Therefore, might be an optimum candidate for industrials applications. In the films produced with cellulosefiber mixtures, the presence of cracks and empty spaces increased with an increasing proportion of the densities respectively and good crosslinked of particles in the products.

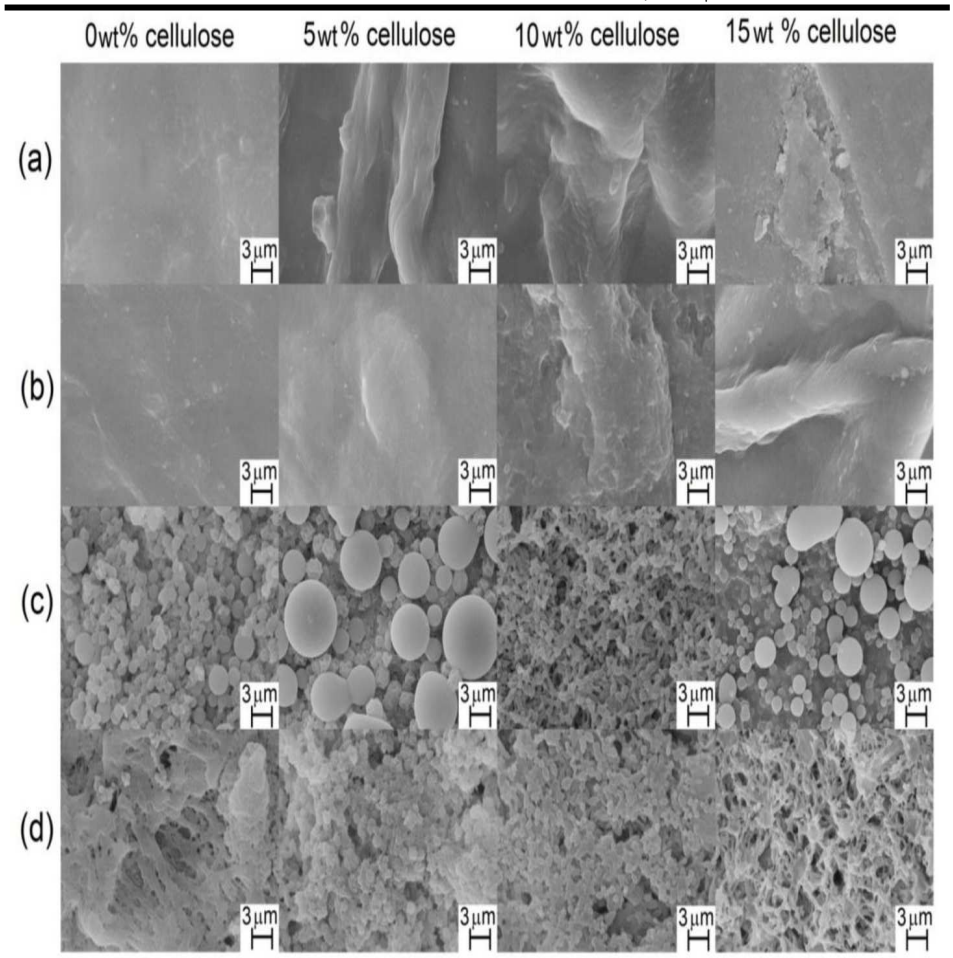

Figure (3.1):SEM micrographs of the surface sections of CA form cotton linter and cellulose with additives: (a, b, c, and d) cross link polymer with (0, 5, 10, and 15) % w/v respectively. Scale bar: 3 (µm).

3.2 Infrared Spectroscopy Testing (IR):

Figure (3.2) present the FTIR spectra of CA produced from cotton linters. It can be seen that identical characteristics peaks appear in the two samples; these indicate that the CA produced from cotton linters has the same function groups. The dominant absorption peaks around 3403 and 2916 cm^{-1} are attributed to the stretching vibrations of -OH

group and the C-H bond in $-CH_2$ respectively. The observations of these peaks provide evidence of acetylating.

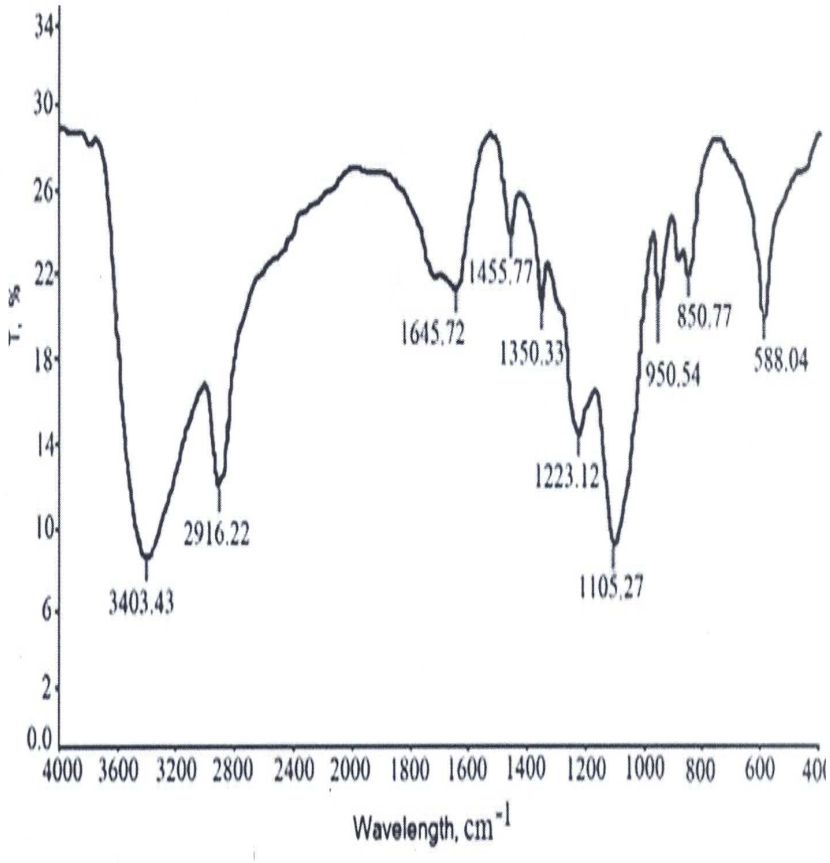

Figure (3.2): FTIR spectra of CA produced from cotton linter.

3.3 Mechanical Testing:

As mentioned before, the main interest in the production of cotton linter/Sudanese Gum Arabic and polyethyleneglycol600were to achieve the materials with better mechanical properties. The investigated mechanical properties, i.e., tensile strength, as well as strain at break were found to depend on the amount of modification. As expected,

cross linking led to an improvement in the tensile strength. Based on these analyses, the composition of biodegradable plastic and modification were considered the optimum conditions for the preparation of cross linking biodegradation. The irregular arrangement within cotton lintermodifiedSudanese Gum Arabic and polyethyleneglycol600(Table 3.1) has strong influence on mechanical properties. Independent of the modification, the values for tensile strength of the films produced from crosslink biodegradable plastic mixture was significantly different varied as a function of the cotton linterconcentrations. To examine the correlation between mechanical property changes and crosslink polymer, constant strain-rate tests were performed on the modified polymer in order to determine their elastic moduli. Representative stress–strain curves of the modified degradable plastic are presented in Tables (3.1). These results displayed the ability of cotton linterconcentration to individually affect the modulus of crosslink modification plastic. Based on the mechanical property results for our bio composite plastic which are able to attain high tensile strength, it is concluded that there is an opportunity for applications as potential candidate for industries.

Table (3.1): The results of tensile test for sample of CA produced from cotton linters.

Product	**Load max (N)**	**Stress max (Mpa)**	**Elongation at break (%)**	**Moedulos (young) (Mpa)**
CA from cotton	13.85	118.96	45	1170.2

3.4 Effect of Acid on cellulose Acetate:

Tables (3.2), (3.3) and Figure (3.3) were shown the influence concentration of sulfuric acid on weight loss of CA produced cotton linters. The increasing concentration of

sulfuric acid and decreasing the weight of cotton linters increasing the weight loss.

Table (3.2):Effect of different concentrations of sulfuric acid on weight loss of CA produced cotton linters.

Time(day)	Weight %			Weight loss %		
	Conc. 10%	Conc. 20%	Conc. 30%	Conc. 10%	Conc. 20%	Conc. 30%
0	10	10	10	0	0	0
1	9	8.5	7.5	1	1.5	2.5
2	7	6	5	2.2	2.9	3.3
3	5.5	4	3	2.9	3.3	4
4	3.5	2	1	3.6	5	6.6

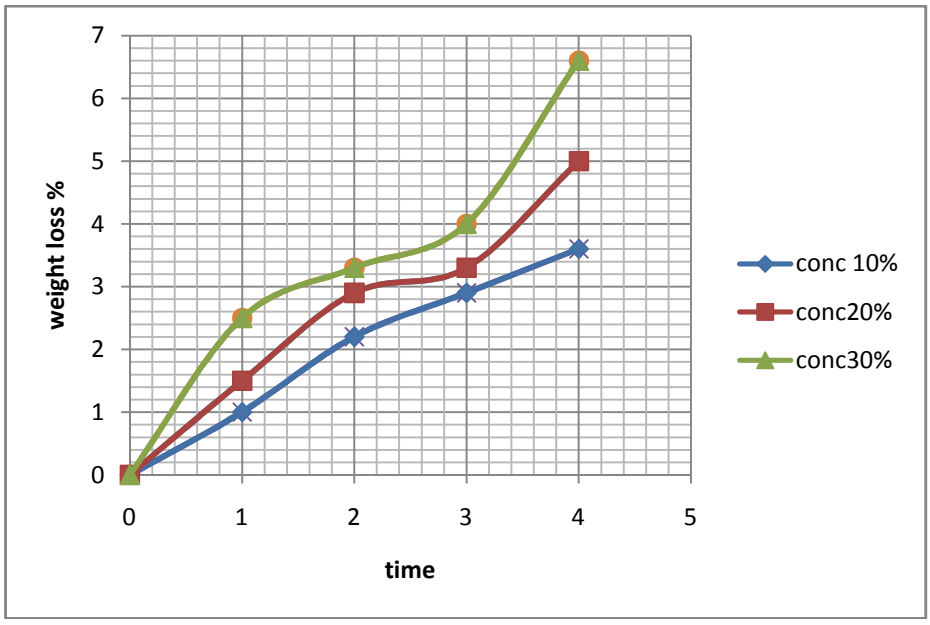

Figure (3.3): Effect of different concentrations of sulfuric acid on weight loss of CA produced cotton linters.

Figure (3.4): show the results from the effects of different concentrations of sulfuric acid at on CA produced from cotton linters.The weight loss of CA, produced from cotton linter, had been increased by increasing the concentration of sulfuric acid from (10, 20 and 30) %, then, the weight loss of CA became reduced at 30% sulfuric acid concentration. These results can be explained by the fact that, by increasing acid concentration from 10% to 20%, the acid content increased and, hence, the weight loss increased. However, at 30% acid concentration, there was a reduction in the water content which promoted the bonding rupture by acid and gave a lower weight loss (2.5%) of CA produced from cotton linters. These results could be due probably to the high stability of chemical crystalline structure and bonding of CA from cotton linters.

Table (3.3): Effect of different concentrations of sulfuric acid on weight loss of CA produced cotton linters.

time	Weight			Weight loss %		
	Conc.10%	Conc. 20%	Conc. 30%	Conc.10%	Conc. 20%	Conc. 30%
0	10	10	10	0	0	0
1	8	7.5	7	2	2.5	3
2	6	6	5	2	2	2.9
3	4	3.5	2.5	3.3	4.2	5
4	2.5	2	0.5	3.8	4.3	8

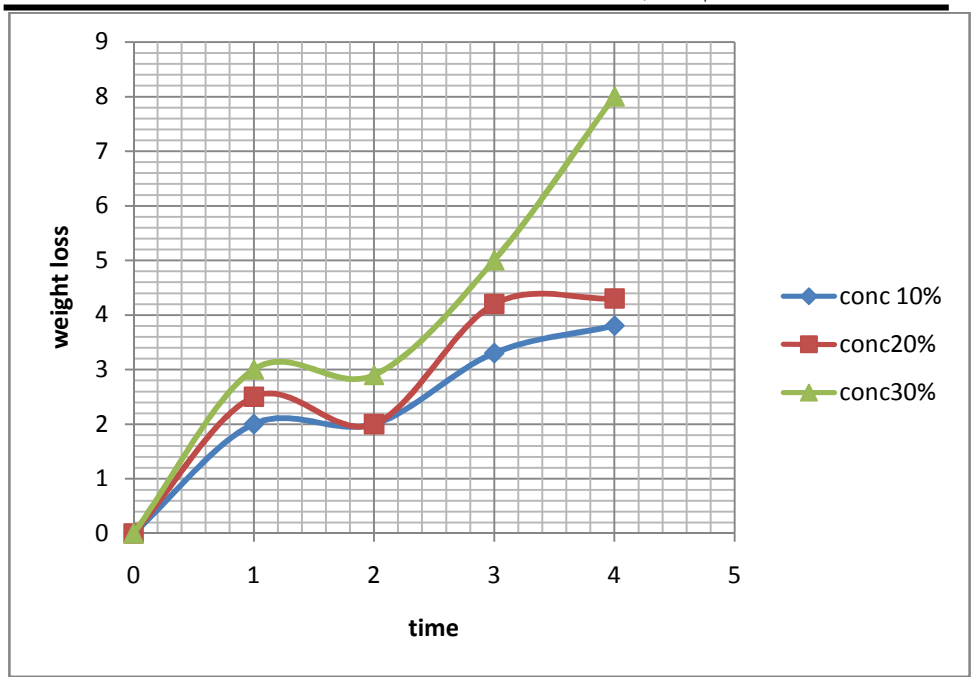

Figure (3.4): Effect of different concentrations of sulfuric acid on weight loss of CA produced cotton linters.

3.5 Effect of Alkalis on Cellulose Acetate

As illustrated in Table (3.4) and Figure(3.5) the weight loss of CA produced from cotton linters increased as the concentration ofNaOH increased, also it was increased over time. The effect of time was less pronounced for more concentrated solutions.

It is clear from the results that the resistance of CA, produced from cotton linters to alkalis was nearly the same.

Table (3.4): Weight and weight loss of sample of CA from cotton linter.

Time/day	Weight				Weight loss %			
	Conc. 10%	Conc. 20%	Conc. 30%	Conc. 40%	Conc. 10%	Conc. 20%	Conc. 30%	Conc. 40%
0	10	10	10	10	0	0	0	0
1	9.5	9.3	9	8.8	5	7	10	12
2	9	8.7	8	7.5	5.3	7	11.1	14.8
3	8.4	8	6.9	6	6.7	8.1	13.8	20

4	7.8	7.1	5.9	4.7	7	11.3	14.5	21.7
5	7	6.2	4.8	3.6	10.2	12.3	18.7	24.5
6	6.2	5	3.9	2.5	11.5	19.4	18.9	31
7	5	4	2.8	1.4	19.4	20	28.2	44

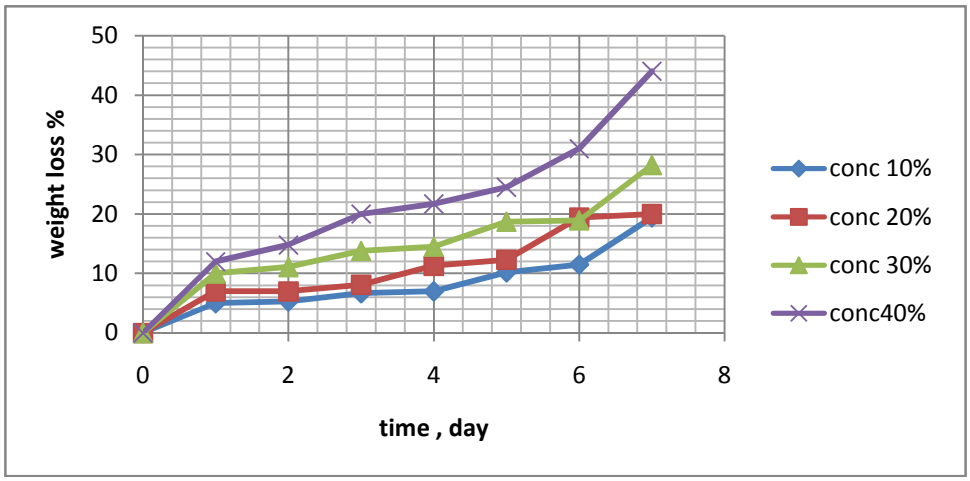

Figure (3.5): Effect of alkalis on cellulose acetate cotton linter.

3.6 Microbiological Test:

Figure (3.6) present the results of biodegradation using aerobic organism for cotton linters and the difference between using polyethylene glycol and Sudanese Gum Arabic (plasticizers).Table (3.5) showed the weight loss of CA from cotton using plasticizer (polyethylene glycol and gum Arabic). It is clear from the Figure (3.6) that, in the case of biodegradation tests from aerobic organism, CA lost 5% & 8% of its weight after the first three days by using polyethylene glycol and Sudanese gum Arabic (plasticizers), then the percentage of weight loss continued to increase over time until it reached 55% & 63% after 10 days for CA produced from cotton linter.

Table (3.5): Weight loss of CA from cotton linters using plasticizer (polyethylene glycol and gum Arabic).

Time\day	weight		weight loss %	
	Poly etth-glycol	Gum Arabic	Poly ethy-glycol	Gum Arabic
0	10	10	0.0	0.0
1	9.8	9.6	2.0	4.0
2	9.5	9	3.1	6.3
3	9	8.3	5.3	7.8
4	7.9	7	12.2	15.7
5	6.4	5.8	19.0	17.1
6	5.1	4.6	20.3	20.7
7	4	3.5	21.6	23.9
8	2.9	2	27.5	42.9
9	2	1.1	31.0	45.0
10	0.9	0.4	55.0	63.6

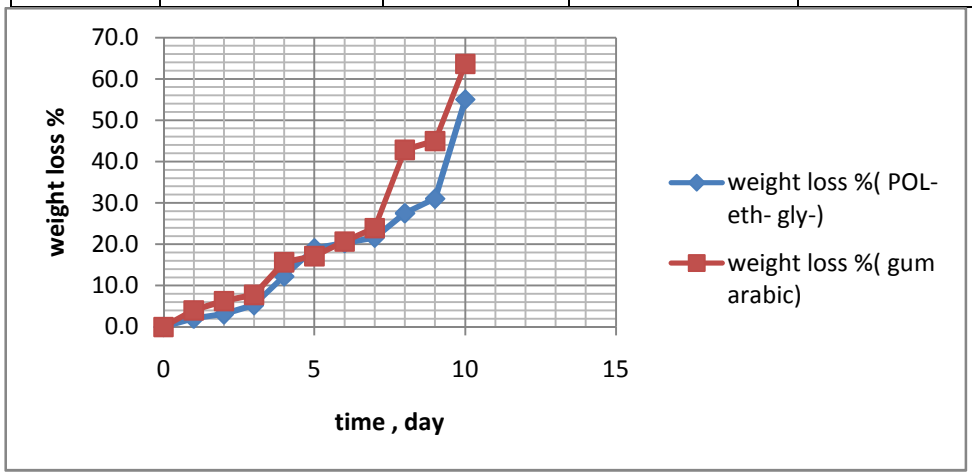

Figure (3.6):Biodegradation tests from aerobic organism for CA from cotton linters using plasticizer (polyethylene glycol and gum Arabic).

4.1 Conclusion:

In this study engineered a biodegradable plastic with crosslinked structures based on cotton linterusing polyethylene glycol and Sudanese gum Arabicas plasticizer. To our knowledge, this research presented a new idea for the bio-macromolecular polymer and better results from previous research of biodegradable plastic with controllable elastic moduli, and degradation rates. The biodegradablecrosslinked plastic showed the good mechanical properties as evaluated from tensile tests, strongest and fastest decomposing, no cytotoxic effects and excellent compatibility. The size and arrangement of these pores were the presence of cross linking agents.The effects of acid, alkali, salts on cellulose acetate of the biodegradable plastic decompose in a compost bin for 2 weekswere investigated. The addition of Sudanese gum Arabic as important factor related to the product properties, it seems that the biodegradable plastics were doing really good comparing with the conventional plastic. This information about biodegradable plastics can become very useful in the future because the biodegradable plastics could be sustainable for the environment and can be made and used efficiently by us. Currently the biodegradable plastics are not cheap and recyclable; however it reduces oil consumption and greenhouse gases from production, biodegradable plastics is a possible solution to replacing petroleum plastics. With more research, could successfully make plastics from more sustainable resources and also make them recyclable as well.

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