

## BIOPLASTICS PRODUCTION FROM STARCH AND CHITOSAN BLENDS

### Produção de bioplásticos a partir de blendas de amido e quitosana

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### ABSTRACT

Plastics are used in many consumer goods, its raw material comes from a non-renewable resource, oil, and its disposal causes accumulation of waste due to its long degradation. An alternative are bio based and biodegradable plastics, which are highlighted in the scientific community. The bio based and biodegradable plastics can be produced from starch which is a polysaccharide synthesized by plants. In order to evaluate the effect of the reactants on the bioplastics characteristics, and through the analysis of previous publications, it was possible to produce a polymer blend using chitosan, which can be obtained from the carapace of shrimps that come from inappropriate disposal of the processing waste. To observe the behaviour of the bioplastic, based on variation of the reactants, the volume of glycerin was varied between 0 to 4 mL, the concentration of acetic acid was varied between 2 to 15%, and the concentration of chitosan was varied between 0 to 100%. It was possible to observe that the glycerine has an important role at the flexibility of the film, the acetic acid influences on the consistency, elasticity and shape, and the chitosan influences on the stiffness and thickness. The sample material showed satisfactory characteristics such as color, density, biodegradability, and odour, in addition, the samples presented total integration of the chitosan with the starch.

**Keywords:** bioplastics, glycerol, chitosan.

### RESUMO

Os plásticos são utilizados em muitos bens de consumo, sua matéria-prima provém de uma fonte não renovável, o petróleo, e o seu descarte causa acúmulo de lixo devido ao longo tempo de degradação. Uma alternativa são os bioplásticos e biodegradáveis que estão em grande ascensão no mundo científico, podendo sua produção partir do amido, que é um polissacarídeo sintetizado pelos vegetais. No intuito de avaliar o efeito dos reagentes nas características do bioplástico, e através do estudo de publicações anteriores, será produzida uma blenda polimérica do amido com quitosana, obtida a partir da casca proveniente do descarte inadequado do resíduo do beneficiamento do camarão.

Para observar o comportamento do material, foram aplicados diferentes volumes de glicerina, entre 0 a 4 mL, ácido acético em diferentes concentrações, entre 2 a 15% e diferentes concentrações de quitosana, entre 0 a 100%. Foi possível observar que a glicerina tem um importante papel na flexibilidade do filme, o ácido acético influencia na consistência, elasticidade e forma, e a quitosana influencia na rigidez e espessura. O material de amostra apresentou características específicas como: cor, densidade, biodegradabilidade e cheiro, satisfatórios, além de total integração da quitosana com o amido.

**Palavras-chave:** Bioplástico, Glicerol, Quitosana.

## INTRODUCTION

Natural resources have an important role in the growth of Gross Domestic Product (GDP) of any country, as well as in social and economic development. There is a worldwide trend to use these resources through new technologies and to develop new products. As a result, there is the creation of new jobs, income generation; therefore, improving the standard of living of the people (GUIMARÃES, 2010).

Plastic materials are present in the daily lives of every person, like household items, materials technology, toys and medical products. This expansion and diversity in the use of plastics is due to the convenience they provide and the low price compared to other materials. These are obtained from naphtha, which is a by-product of petroleum refining, used on a large scale in petrochemical industry (PIATTI, 2005).

Conventional polymers (commonly called plastic) are obtained from the mixture of organic compounds, named as petroleum. Starting with the petroleum, which passes through a fractional distillation process to obtain naphtha, where the monomers come from. These, when subjected to a polymerization process, combine to form giant molecules, the polymers (PIATTI, 2005).

However, there is the problem of excessive use of petroleum, which is allied to the future depletion of its reserves. The major environmental impacts caused by the extraction and refining processes, the petroleum shortage and its price increases, are some environmental and socioeconomic factors that are related to the interest in the production of biopolymers (BRITO *et al*, 2011).

In addition to these factors, there is the issue of non-biodegradability of most polymers produced from petroleum, which contributes to the accumulation of plastic waste without proper destination (BRITO *et al*, 2011).

Polymers produced through natural and renewable sources have featured among the possible materials used to produce plastics. Considering that, they have some advantages, such as being biodegradable, biocompatible, non-toxic and high availability. Thus, biopolymers emerge as a possible solution to avoid the use of non-renewable raw materials (ZIA *et al.*, 2015). Due to its biodegradability, low cost and high availability, starch is an alternative to replace petroleum derivatives in the production of plastics, for passing through suitable processes becomes a compound called thermoplastic starch, which can be used in replacement of naphtha (PIRES *et al.*, 2009).

However, this application is limited due to poor mechanical properties such as high fragility. One way of overcoming this drawback is to produce a polymer blend of starch with chitosan (Wurzburg *et al*, 1986). Combine polymers is a simple method used to improve the properties of polymeric materials (Li *et al*, 2013).

The ability to maximize the pros and reduce the cons from these blends can result in a significant increase in the quality of bioplastics, reducing costs and obtaining a material with improved physical properties and applications in various industries.

Chitosan is a high molecular weight polysaccharide composed of D-glucosamine units and an amino free group. This polymer is obtained by deacetylation of chitin (Tuhin *et al*, 2012). Both are considered non-toxic, biocompatible, biodegradable and produced by renewable natural source polymers such as cell walls of some fungi, exoskeleton of insects, algae, diatoms and exoskeletons of crustaceans (shrimp, crab, lobster and krill) (ANDRADE *et al*, 2010).

The presence of the amino group differs chitosan from chitin, and gives this polymer many peculiar properties. The amino group can be protonated, providing solubility in acidic solutions. Due to the presence of the amino group, chitosan complex is also present in several species and can be used for various applications. (CROISIER; JÉRÔME, 2013)

The use of chitosan in the production process also acts as an alternative to solve the problems caused by improper disposal of waste from the shrimp processing. It consists of chitin, protein, calcium carbonate, and can cause social problems, having unpleasant odor, attracting insects and causing harm to human health (ANDRADE *et al*, 2012).

Acting as a plasticizer, in order to improve the mechanical characteristics of the material and decrease the melting point of the starch granules, glycerin is used, which is in constant rise in the market. It is estimated that worldwide production glycerin reach 1.2 million tons, due to the increasing production of biodiesel (MOTA *et al*, 2009).

The objective of this paper is to produce blends of chitosan and starch, and study the behavior of the produced samples, based on variations of the proportion of the reactants, to achieve the best preparation method available.

## MATERIAL AND METHODS

### OBTAINING OF POLYMER BLENDS

The production process of the blends were based on previews similar studies, such as S. Santacruz, (2015) and Dan Xu (2015). The methodology applied on those articles were tested with variations. The presented process of production reported was the one that showed the best result for the required application.

In order to realize the following experiment it was used chitosan that was obtained from the carapace of shrimps *Litopenaeus schimitti*, and commercial corn starch Maizena®, and the following equipment: Magnetic stirring IKA® C-MAG HS 7, laboratory oven GEHAKA G4023D and analytical balance SHIMADZU AUX220. Two procedures were performed at the same time. The first was the formation of starch blends; resultant from the mixture of starch and water in a constant magnetic stirring at 50°C, the system was stopped when the solution had a gelatinous and consistent appearance. The second procedure was the solubilization of the chitosan in acetic acid; this is acquired in constant magnetic stirring at 50°C. After reach the required consistency in both of the systems, the two blends were mixed and glycerin was added. This method was the standard adopted for all samples, the blends were observed proportionally according to Table 1, given that were used in total 5 grams of chitosan and starch.

**Table 1.** Quantification of polymer blends

Percentage (%)	0	25	50	75	100
Chitosan (g)	0	1,25	2,5	3,75	5
Starch (g)	5	3,75	2,5	1,25	0

## OBTAINMENT OF THE BLEND 100% STARCH / 0% CHITOSAN

The formation of the polymeric "blend" 100% starch and 0% chitosan was possible due to heating, addition of glycerin and acid to the starch. The heating is necessary, because the starch granules are insoluble in cold water due to the strong hydrogen bonding that keeps together its chains. However, in the presence of water and heating, the water is incorporated into the structure of the granule and more soluble components such as amylose dissociate and diffuses out of the pellet, this process is called gelatinization, and occurs at about 60°C (CORRADINI *et al*, 2007).

After gelatinization occurs the retro gradation, where molecules, especially amylose, are oriented parallel, approaching enough to form hydrogen bonds. This phenomenon results in reduced volume, increased firmness of the gel produced and reduction of the polymer affinity for water, thus explaining the formation of stable and flexible films by gelatinized starch. These films were obtained by a technique known as casting, where the solution was applied onto a petri plate, and then carried into the drying oven (MALI *et al*, 2010).

The plasticizer used was glycerin. The use of glycerin is necessary because the plasticizers reduce intermolecular forces and increase the mobility of polymers chains with reduction of possible discontinuities and brittle zones (WARRIOR; MENEGUELLI, 2009).

The acid addition was also a factor of great importance for the formation of the plastic due to hydrolysis caused by the hydrochloric. The acids first hydrolyzes the amorphous region before attacking the crystalline regions, amylose and amylopectin are simultaneously hydrolyzed to smaller molecules, facilitating the formation of linear chains and subsequent formation of the plastic (MALI *et al*, 2010).

## DETERMINATION OF THE AMOUNT OF GLYCERIN IN THE POLYMER BLENDS

This method was employed in order to verify the influence of glycerin in polymer blends. A standard quantity of starch, chitosan and acetic acid were established and only the amount of glycerin used was varied. The different proportions were named according to table 2.

**Table 2.** Classification of samples

Samples	A1	A2	A3	A4	A5
Glycerin (mL)	0	1	2	3	4

## DETERMINING THE AMOUNT AND CONCENTRATION OF ACETIC ACID IN POLYMER BLENDS

This analysis was conducted to verify the possible influences of acetic acid in polymer blends, and to improve the reaction avoiding waste and / or damage of the sample. The variations in each ratio are shown in Table 3.

**Table 3.** Solution of Acetic Acid

Chitosan	25%		50%		75%		100%	
	V(mL)	Conc. (%)	V(mL)	Conc. (%)	V(mL)	Conc. (%)	V(mL)	Conc. (%)
<b>Method A</b>	50	5	100	5	150	5	200	5
<b>Method B</b>	12,5	15	75	15	112,5	15	150	15
<b>Method C</b>	25	2	50	2	75	2	100	2
<b>Method D</b>	6	10	6	10	-	-	-	-
<b>Method E</b>	50,6	6	101,3	6	151,9	6	202,5	6

## EVALUATION OF MECHANICAL PROPERTIES OF POLYMER BLENDS

The mechanical properties were evaluated through qualitative analyses. Based on previous published articles and the objective of the study, qualitative analyses were suitable to be applied. The mechanical tests, accordingly to ASTM standards are in progress at the moment.

## EVALUATION OF DEGRADATION OF POLYMER BLENDS

This property were evaluated by placing the samples in a soil with low content of clay and organic materials in order to find out bioplastic behavior when in direct contact with the soil.

Biodegradation tests are used to predict the time and how much decomposition of chemicals in the environment extends. The biodegradability is recognized as environmental safety indicator and test conditions should be as close as possible to reality. (SILVA *et al.*, 2011).

## RESULTS AND DISCUSSION

### VARIETIES OF POLYMER BLENDS

It is extremely important to know the ability of the material to withstand the stress to which they will be subjected during transport, storage and handling (ALJAWISH *et al.*, 2016). For this, several different tests were carried out to establish which methodology that showed better results and that is compatible with the conditions available for the development of the project. Based on this methodology it was possible to obtain a material, which generally have reasonable quality in relation to the tensile strength and elasticity.

Seeking to study the behavior of the material, variations related to the proportion between starch and chitosan were made. All samples produced during the project development have the same thickness and diameter. The ratios studied were the following: 25%, 50%, 75% and 100% chitosan.

### DETERMINATION OF THE AMOUNT OF GLYCERIN IN THE POLYMER BLENDS

To make it possible to compare the results, it was adopted a range from 0 to 3, with 0 being equal to no elasticity value and the value 3 equivalent to greater elasticity found in the samples.

As a result, it is observed that all the samples, regardless of their proportion of starch/ chitosan, could be produced, this is due to intermolecular interaction between the  $\text{NH}_3^+$  of chitosan in acid and  $\text{OH}^-$  available in the starch when it is gelatinized (Xu et al, 2005). With the increase in chitosan concentration, it was possible to notice a decrease in elasticity and a darkening on the color of the material.

In order to improve the mechanical characteristics of the samples, variation of the amount of glycerin used in the production process was studied. The following table presents the obtained results. The A1 nomenclature referring to the method without the addition of glycerin, A2 with the addition of 1 ml of glycerin, A3 with the addition of 2 ml, with addition of A4 and A5 3 ml by the addition of 4 ml of glycerin.

Using the obtained samples was possible to observe a trend in increasing elasticity proportional to the increased amount of glycerin, and that the flexibility of the film does not exist when using the plasticizer is not used. It was not possible to withdraw some of the sample of petri plates. In general, these samples had little or no amount of glycerin, so this result was attributed to lack of glycerin and also a possible excessive heating.

With the increase of the amount of glycerin, flexibility is also increased. However, it was observed that there is a point where the plasticizer affects negatively the quality of the samples as the same becomes very soft and brittle.

## **DETERMINING THE AMOUNT AND CONCENTRATION OF ACETIC ACID IN POLYMER BLENDS**

By analyzing method A, that had the best result, it was made the method E, with the purpose of increasing the thickness of the final product through the water reduction (-25%), increase in the mass amount of chitosan (+25%) and increasing volume of acetic acid (+25%). This method presented the best results, with excellent characteristics without hatches, viewing in Table 5. The methods B, C and D were made varying concentrations of acetic acid and water from the quantities used in the methods A to E (Xu et al, 2005) until it reached the most favorable method of producing bioplastic (E).

## **DEGRADATION'S EVALUATION OF POLYMER BLENDS**

Observing the behavior of the blends in fortnightly periods, it was noticed that at the second check the blends presented slightly cracked and with a moisture content much lower than the original.

## **CONCLUSIONS**

On the methodology used in obtaining the polymer blends it is possible to conclude that it can be used to obtain the bioplastic samples, since it has proved effective. In relation to the amount of glycerin used in the production of the samples it was possible to observe a trend in increasing elasticity proportional to the increased amount of glycerin, and that the flexibility of the film does not exist this plasticizer is not used. Moreover, there is a point where the plasticizer affects negatively the quality of the samples as the same becomes very soft and brittle. In determining the amount and concentration of acetic acid it was noted that the blends show no hatches and embody features of elasticity, consistency and shape at higher concentrations.

The blends of the bioplastic, with the addition of chitosan sample, reduces stiffness and thickness proportionately causing biodegradation of these directly on the ground. The higher is the amount of chitosan, the faster degradation in the soil occurs.

The evidence shows that the chitosan bioplastics has great potential and innovation, due to the residual raw material used and the great characteristics of the final product obtained.

**Table 4.** Comparison of samples with different proportions of chitosan / starch

Scale (0-3)	25%	50%	75%	100%
A1	Elasticity 0	Elasticity 0	Elasticity 0	Elasticity 0
	Inelastic	Removal Not Made	Inelastic	Removal not made
	Uneven Distribution	Regular Distribution	Regular Distribution	Regular Distribution
A2	Elasticity 1	Elasticity 1	Elasticity 1	Elasticity 1
	Flexible	Flexible	Removal Not Made	Flexible
	Uneven Distribution	Regular Distribution	Regular Distribution	Uneven Distribution
A3	Elasticity 2	Elasticity 2	Elasticity 2	Elasticity 2
	Flexible	Flexible	Flexible	Flexible
	Uneven Distribution	Regular Distribution	Uneven Distribution	Uneven Distribution
A4	Elasticity 2	Elasticity 2	Elasticity 2	Elasticity 2
	Flexible	Flexible	Flexible	Flexible
	Uneven Distribution	Regular Distribution	Uneven Distribution	Uneven Distribution
A5	Elasticity 3	Elasticity 3	Elasticity 3	Elasticity 3
	Flexible (Breakable)	Flexible	Flexible	Flexible
	Uneven Distribution	Uneven Distribution	Regular Distribution	Uneven Distribution

**Table 5.** Comparative samples of different proportions of chitosan

Method A	Method B	Method C	Method D	Method E
Small Hatches	Brittle	Gelatinous	Net	Consistent

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