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ECONOMIC-MECHANICAL PERSPECTIVES OF THE USE OF BIOFILMS PRODUCED FROM ORANGE PEEL WASTE MODIFIED WITH GRAPHENE

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Abstract: Globally, the production of synthetic polymers doubled from 2000 to 2019, reaching 460 million tons, which represents 3.4% of global greenhouse gas emissions. This is why we seek to replace synthetic polymers with biopolymers, made from organic solid waste that lead to sustainability and sustainability in processes at an industrial level. This work aimed to study the mechanical and economic advantages of producing biopolymers from orange peel modified with graphene. With respect to properties such as: tensile strength, water vapor permeability and water solubility, there were no significant differences with and without graphene. The percentage of elongation in biopolymers with graphene was favored 2.3 times and the Young's Modulus was 2.1 times higher in biopolymers without graphene. In the economic study, it was determined that the sales price of biopolymers without and With graphene was 12 and 1000 times higher than the sales price of synthetic polymers, however, when considering the cost of the environmental impact that is reflected for a government In the disposal and storage of waste, the cost of synthetic polymers rose from a thousand to a billion times more depending on the time it takes for the polymer to degrade, resulting in an opportunity cost for biopolymers that takes up to 5 years. in degrading.

Keywords: synthetic polymers, biopolymer, economic perspective

INTRODUCTION

Food packaging is a conservation strategy that continues to grow and although it can be done using cardboard, glass and metal, plastics have displaced these materials due to the properties they present and that they are capable of extending the useful life of many foods and They prevent the loss of products due to contamination.

Approximately 50% of plastics are destined for single-use applications, such as food packaging, accelerating waste generation. In recent years, the plastic industry has had a great influence on environmental pollution problems and is the one with the greatest growth in production.

Biopolymers are natural compounds synthesized by living beings, which come from various biological groups such as plants, algae, fungi, bacteria and animals. Currently they are combined with synthetic molecules, impacting their resistance and flexibility. A biodegradable packaging is defined by the American Society for Testing and Materials (ASTM) as one that is capable of decomposing into carbon dioxide, methane, water, inorganic compounds or biomass, with the dominant decomposition mechanism being the enzymatic action of microorganisms and that the resulting products can be obtained and measured in a determined period of time (ASTM, 2005).

The biodegradable plastics market currently has an application in flexible packaging, rigid packaging, automotive and assembly operations, agriculture, construction, textiles, electricity and electronics. The size of this market is estimated at more than 1,220 thousand tons in 2020, expected to register an annual growth rate (CAGR) of more than 16% during the forecast period (2021-2026).

There are various investigations on the manufacture of biopolymers with different materials, this research proposes the manufacture of a biodegradable polymer from orange peel and another biodegradable polymer from orange peel With graphene and thus compare the physical-mechanical properties and barrier, in addition to its economic advantages of its use in the packaging market.

Orange peel was chosen because it contains cellulose fibers, pectin and essential oils. The use of pectin as a polymer to obtain bioplastic is due to the fact that it is an abundant, non-toxic and biodegradable raw material. Another of the fundamental reasons for choosing this raw material is that Mexico has fifth place in the world in orange production (SAGARPA 2018). The amount of processed orange represents up to 85% and the peel represents 45 to 60% of the weight of the fruit. Graphene was used as an additive due to its physical and bactericidal properties, capable of inhibiting the growth of microorganisms, making it a potential substrate for the food industry.

PLASTICS

Polyethylene terephthalate (PET) bottles are often the safest way to transport liquids and food, in addition to containers based on expanded Polystyrene that are involved in a type of polymer where the ease and practicality of the product is observed (Webb, 2013).

The large-scale production of soft drinks, carbonated waters and bottled waters in Mexico has one of the first places of consumption worldwide (average per capita consumption of 431 ml/day). Packaging materials are PET, glass and aluminum. The container that is most used is non-returnable PET, its production in the market is very significant (65.8%) followed by glass (11.9%) and aluminum (6.6%) containers (National Institute of Ecology, 2020). Table 1 shows the life time of different plastic utensils after being used.

Plastic bags	20 years
Plastic cups	50 years
Plastic bottles	450 years
Fishing nets	600 years

Table 1 Estimated duration of physical decomposition of plastic waste in the sea

Source: National Institute of Ecology and Climate Change 2019-2020

Globally, plastic production doubled from 2000 to 2019 and amounted to 460 million tons, due to its various uses in food, beverage and industrial packaging, due to its barrier properties, "permeability" (Muñoz, 2012). This property is what makes plastics attractive. Plastic represents 3.4% of global greenhouse gas emissions, reaching a global waste generation of 353 million tons in 2019. Almost two-thirds of this waste comes from plastic with a useful life of less than five years, 40% of which is derived from packaging, 12% from consumer goods and 11% from clothing and textiles.

Only 9% of plastic waste is recycled, 19% is incinerated, 50% is used as landfill and 22% bypasses waste management systems and ends up in uncontrolled landfills and is burned in pits. open or end up in terrestrial or aquatic environments, especially in poorer countries (Global Plastic Outlook, 2020).

In Mexico, the plastic industry has a production value of 30,000 million dollars and participates with 2.6% in the GDP of the manufacturing sector, with nearly 4,100 companies that participate in the production of plastics for general consumption, containers and packaging, construction, electronic, automotive, agricultural and medical, generating 260,000 direct jobs. 56% of PET containers are recycled, investing around 340 million dollars in 16 recycling plants in the country and more than 90 million dollars in promoting collection and environmental education in the last 17 years (Secretariat of Economy, 2021).

Furthermore, in Mexico and other parts of the world, legislation regarding the use of plastics has been changing.

BIOPOLYMERS

Natural polymers or biopolymers are compounds synthesized by living beings and fulfill biological functions (such as proteins, nucleic acids), structural (polysaccharides) and defense or maintenance of aqueous activity (biofilms). Natural sources of biopolymers cover various biological groups (algae, plants, animals, bacteria and fungi). Currently, biopolymers can be combined with synthetic molecules, impacting their resistance and flexibility (Velde and Kiekens, 2002).

Biopolymers offer an advantage over synthetic materials given their biocompatibility, biodegradability, low antigenicity, and that they are renewable (Sahana & Rekha, 2018).

Biopolymers can be classified given their origin and functionality. Based on the charge of their surfaces, biopolymers can be classified as anionic (tragacanth, arabic, karaya, xanthan, carrageenan, gellan, agar, pectin and alginate gums), cationic (modified guar gum), non-ionic (tamarind gum, Arabica, cellulose and carob).

Another classification of biopolymers is given based on their linear structure (pectin, cellulose and carob), or branched (gum arabic, guar, karaya and amylopectin (Mohammadinejad et al., 2020).

A biodegradable packaging is defined by the ASTM in Mexico as one that is capable of decomposing into carbon dioxide, methane, water, inorganic compounds or biomass, with the dominant decomposition mechanism being the enzymatic action of microorganisms and that the resulting products can be obtained and measured in a certain period of time, (ASTM, 2005).

For its part, the bioplastics and biopolymers market was positively impacted by COVID-19 in 2020, increasing the demand for flexible packaging, which represented more than 45% of bioplastics, due to the increase in demand for consumer products. personal, healthcare, pharmaceuticals, packaged food and beverages.

Bioplastics are a renewable and sustainable option for a variety of industrial uses. According to European Bioplastics, in 2020, 47% of global bioplastics production was used in packaging applications. According to Bioplastics Market Report (2020), the bioplastics market will grow by 13.1% from 2022 to 2029, reaching 25.93 billion dollars by 2019. Currently the main companies producing bioplastics are: BIOTEC (Germany), Braskem S.A. (Brazil), BASF SE (Germany), Biome Bioplastics Limited (U.K.), DuPont de Nemours, Inc. (U.S.), AKRO-PLASTIC GmbH (Germany), Saudi Basic Industries Corporation (Saudi Arabia), FKuR Kunststoff GmbH (Germany), Novamont S.p.A. (Italy), Plantic Technologies Limited (Australia), Futerro SA (Belgium), PTT Global Chemical Public Company Limited (Thailand), Showa Denko K.K. (Japan), Solvay SA (Belgium), Mitsubishi Chemical Holdings Corporation (Japan), Teijin Limited (Japan), Toray Industries, Inc. (Japan), Total Corbion PLA (Netherlands), Toyota Tsusho Corporation (Japan), and Green Dot Bioplastics, Inc. (U.S.) (Bioplastics Market Report, 2020).

ORANGE PEEL

Orange peel works as a great option to produce biopolymers because it contains cellulose fibers, pectin and essential oils.

Orange production took Mexico to fifth place in the world, with an average volume of 4.2 million tons per year, which were marketed both in the domestic market and in international destinations (SAGARPA, 2020). The value of production is estimated at more than 6 billion pesos, with an annual per capita consumption of 37.1 kilograms and contributes 22.5% of the volume of fruits that are produced in the country (SAGARPA, 2020).

The amount of orange processed by the industry represents up to 85%, the pulp extracted from the fruit is used for the preparation of concentrates, pulps, nectars and juices. The peel represents approximately 45 to 60% of the weight of the fruit, generating approximately 2 to 2.5 million tons of waste per year.

The waste material of oranges consists mainly of peels, seeds and capillary membranes from which citrus flours, citrus pectin, essential oils, pigments and special citrus products can be obtained; as well as bioactive compounds that have beneficial effects on health, such as fiber, and polyphenols, especially flavonoids.

The use of pectin as a polymer to obtain bioplastics is due to the fact that it is an abundant and non-toxic raw material, in addition to being biodegradable.

Pectins are polysaccharides present in plant tissues, composed mainly of galacturonic acid chains. Pectins have been extracted by different methods from the plant tissues of various fruits, mainly from waste materials such as citrus peels, in which a higher yield has been found (Canteri et al., 2012). Recently, reports have been found of the use of pectins for the manufacture of coatings and packaging films as an alternative to packaging of synthetic origin, with which waste can be used.

GRAPHENE

Carbon is the fourth most abundant element worldwide (after hydrogen, helium and oxygen). In addition to being a polymorphic element, it can exist in three different forms, diamond, graphite and as fullerenes. Graphite is an anisotropic material, which means that its properties, such as thermal and electrical, vary depending on the direction in which they are examined, for example, it is considered an excellent thermal and electrical conductor if we observe it from within the laminar plane. However, these properties decrease when we see it from a perpendicular point of view (because the van der Waal forces are very weak between sheet and sheet. By separating a single sheet of carbon atoms from graphite, graphene is obtained (Chung, 2002).

Graphene is defined as a thin flat sheet of carbon atoms with sp2 hybridization in two dimensions (2D), forming a structure similar to a honeycomb (Kumar & Lee, 2013). It was isolated for the first time in 2004, by physicists Andre K. Geim and Konstantin S. Novoselov, by gluing a piece of tape on the surface of graphite, but it was not until 2010 when graphene began to generate interest. in the rest of the scientists, when its discoverers won the Nobel Prize in physics.

This interest was due to the unique characteristics of the material, such as excellent electrical conductivity, its large surface area, hardness and great thermal conductivity. Furthermore, as it comes from a natural substance such as graphite, it has less environmental risk than inorganic materials (Bunch et al., 2008; Zhu et al., 2010).

Graphene is the strongest material known in nature, stronger than structural steel of the same thickness and harder than diamond, and yet its thickness ranges between 1 and 10 carbon atoms. Because it is so thin and only two of its dimensions can be seen, it is considered a two-dimensional material, the only one that is capable of remaining stable up to the thickness of an atom.

Because it has a size of 50 nm, it is considered a "nanomaterial." Nanotechnology is based on the control of matter at scales between 1 and 100 nanometers and has made great progress in recent years. One of its notable advances is in the biomedical field, with the use of materials with special characteristics such as quantum dots (QD) or carbon nanotubes, used for imaging or cancer treatment. Graphene and its derivatives, graphene oxide, are being studied for their biomedical applications such as FET/FRET sensors, mass spectroscopy, cell differentiation and control of their growth and in the treatment of cancer, among others.

It has elasticity and flexibility properties and is endowed with great thermal and electrical conductivity, which allows it to dissipate heat and withstand intense electric currents without heating up. It is practically transparent, water-repellent and so dense that not even helium gas can pass through it. In addition, it has many other qualities, such as the high mobility of its electrons, a property that increases its potential use in the fast nano devices of the future.

Graphene has incredible mechanical, electronic, chemical, magnetic and optical properties that have made it one of the most studied nanomaterials today.

METHODOLOGY

BIOFILM

The experiments were designed in two stages, establishing the range of concentrations according to a solid weight of 100 g. Since glycerin is the plasticizer, its concentration remains constant (40gr); In the case of orange peel and pectin, there is a relationship between their concentrations (60 g), since orange peel does not contain the necessary amount of pectin to make the film and is compensated by adding a greater amount of pectin. In the first stage, the most appropriate Formulation was defined from orange peel, pectin and glycerin that presents better physical-mechanical and barrier properties. In the second stage, the most efficient film was chosen according to its properties and the effect of the addition of graphene was evaluated.

OBTAINING AND PROCESSING ORANGE PEEL

Orange peel was collected from waste generated by juice stands and the extraction of essential oils. The collected shells were cleaned and dried at 70°C for 2 hours. They were subsequently ground and sieved to a mesh size of 100. The product obtained was stored in glass containers at a temperature of 5°C.

PREPARATION OF BIODEGRADABLE FILM FROM ORANGE PEEL

A total of 5 formulations were tested as shown in Table 2. The orange peel and pectin were mixed by slowly adding each of the ingredients to distilled water (250 ml) previously heated to 60°C, stirring for 5 min at 100 rpm. Having the sample homogeneous, the glycerin was added and kept stirring for 20 min at 600 rpm and a temperature range between 55° - 65°C. After the filtering time had elapsed, 186 ml of the mixture was added to a previously washed and degreased glass square, trying to cover the entire area of the plate evenly, avoiding the formation of bubbles. It was left to dry between 18° - 25°C for 48 hrs.

Formulation	Orange peel (g)	Pectin (g)	Glycerin (g)
1	30	30	40
2	25	35	40
3	20	40	40
4	15	45	40
5	10	50	40

Table 2. Formulations for biofilm formation

PREPARATION OF BIODEGRADABLE FILM FROM ORANGE PEEL AND GRAPHENE

Three formulations were tested, modifying only the graphene concentration (Table 3).

Formulation	Orange peel (g)	Pectin (g)	Glycerin (g)	Graphene (g)
6	20	40	40	5
7	20	40	40	10
8	20	40	40	5*

Table 3. Formulations for biofilm formation With graphene

* Graphene previously mixed with essential oil and added in the form of a spray

The orange peel, pectin and graphene were mixed by slowly adding each of the ingredients to distilled water (250 ml) previously heated to 60°C, stirring for 5 min at 100 rpm. Having the sample homogeneous, the glycerin was added and kept stirring for 20 min at 600 rpm and a temperature range between 55° - 65°C. After the filtering time had elapsed, 186 ml of the mixture was added to a previously washed and degreased glass square, trying to cover the entire area of the plate evenly, avoiding the formation of bubbles. It was left to dry between 18° - 25°C for 48 hrs.

MEASUREMENT OF PHYSICAL-MECHANICAL AND BARRIER PROPERTIES

Elongation and tension tests were done in accordance with ASTM D882, Mexico.

5 strips of 2 cm wide by 12 cm long were cut. The specimens were clamped in the tensile test jaws of a universal vise at a distance of 80 mm between jaws. The tensile test was executed at a head speed of 5 mm/min in duplicate. With the data obtained, Young's modulus and elongation were calculated.

For the water vapor permeability (PVA) tests, a modified standard method from E 96-95 (ASTM 1995) was used and performed in duplicate. Each of the samples was placed in test tubes, calcium chloride previously dried at 200 °C was added 6 mm below the edge of each tube.

The initial weight of the test tube and contents were recorded, and the excess parts of the film were covered with aluminum foil. To prepare the desiccator, 1 vpp of 100 ml with water was introduced, one was attached to two thermometers, one that measured the wet bulb temperature and the other the dry bulb temperature, in order to maintain a relative humidity of 100%. Each tube was placed in the previously prepared desiccator at 100% RH and 32 °C for 24 h. After time, the test tubes were removed and weighed. Finally, the water vapor permeability was calculated with the following equation:

$$RTV\ A = \frac{\text{final weight - Initial weight}}{\text{Time X area}}$$

To obtain the water solubility of the biofilm, two samples for each Formulation were cut into dimensions of 2.5 cm × 2.5 cm and dried in the muffle at 105ºC until constant weight, then placed in 100 ml of distilled water and weighed, then They were placed on an unheated grill with constant stirring for 30 minutes at 100 rpm, the resulting weight was the final weight. The solubility was calculated with the following equation:

$$\text{Solubility (\%)} = \frac{\text{Initial weight - final weight}}{\text{Initial weight}} \times 100$$

ECONOMIC ENGINEERING

In the case of economic engineering, the cost data for raw materials and finished products in Mexico were obtained from SAGARPA (2021), SIAP (2021) and Sigma-Aldrich (2021).

Variable Costs were calculated as follows:

- Operation labor: It was calculated with the following formula wages = (# employees)(minimum wage/day)(day), the number of employees was estimated at 1 for 1 kilogram of the biopolymer.
- Supervision labor: It was estimated from 15% of the operation labor.
- Auxiliary services: It was calculated from the electricity consumption that was estimated at 3.15 KW/h and 4.78 m3/day for 1 kilogram of biopolymer for a process period of 16 hours.
- Maintenance and repair: estimated as 3% of the fixed investment per year. For the fixed investment, the cost of the main equipment was considered, which was $7,250,100 to produce 100 tons of biopolymer.
- Operation supply: it was estimated as 15% of maintenance and repair.
- Fixed Costs were calculated as follows:
- Fixed operating costs, were estimated as 40% of the sum of supervision and operating labor costs.

Fixed investment cost, the cost of the equipment to produce 1 kilogram of biopolymer was considered.

The determination of the real Cost per kilogram of plastic or bioplastic was determined from the following formula:

$$real\ cost = \frac{national\ Cost}{INPC} * 100$$

In the case of synthetic plastics, based on the information collected from INEGI 2021 (Figure 1), data on public spending per capita was obtained in relation to the treatment and storage of urban solid waste (MSW) per year, where It was considered that plastics represented 11% of MSW, and the national consumer price index (INPC) was also taken into consideration, in order to deflate costs.

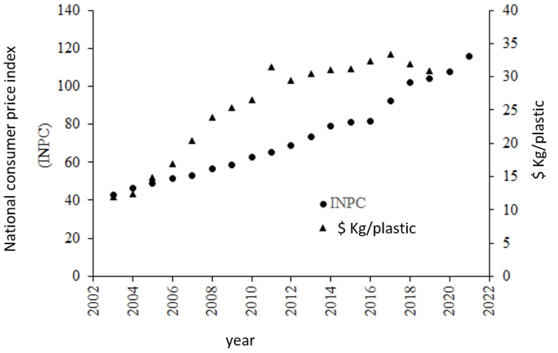

Figure 1. INPC and public spending on plastic treatment and storage per year

From these data, the real Cost was determined with which it was estimated for subsequent years according to the degradation of each of the plastics based on the following model:

$$y = 0.0093\,x^3 - 0.5455\,x^2 + 8.4495\,x + 3.1965$$

Where

y: Actual cost per year

x: year

Determining the real Cost per year according to the years of degradation and deflating it to take it to the year 2021, it was added to the calculated production cost to obtain the real Cost for each polymer.

In the case of the biopolymer, the degradation costs were calculated through the composting process in the year 2021 (Table 4) based on 1 kilogram of biopolymer for a degradation period of 5 years. Likewise, the real cost per year was calculated from the INPC estimate and the cost of the composting process from 2021 to 2025 according to the formula presented for the real cost previously.

Concept	Cost (MNX/year)
Recollection	$38.29
Transportation	$38.29
Control de parameters	$38.29
Shovel	$11.12
Forklift truck	$158.65
Composting construction	$220.84
Total cost per kilo	$505.48

Table 4. Cost of the composting process based on 1 kg of biopolymer

RESULTS AND DISCUSSION

MECHANICAL PROPERTIES

Below are the average results of tensile strength, Young's modulus, percentage of elongation, water vapor permeability and water solubility of the formulations with and without graphene. Table 5 shows the tensile strength data and Table 6 shows the ANOVA statistical analysis. It is observed that in all the formulations tested with or without graphene with a significance level of 0.127, there are no significant differences. Therefore, all the formulation specimens have the same strength before breaking.

Formulation	Tensile strength (N/mm^2)	Standard deviation
1	1.42073	0.06837
2	1.06267	0.20034
3	1.07365	0.35623
4	1.11178	0.28201
5	1.40995	0.22075
6*	1.51093	0.44540
7*	1.48399	0.17589
8*	1.22363	0.51909

Table 5. Tensile strength of biofilms with and without graphene

* With graphene

	Sum of squares	gl	Mean square	F	Sig.
Inter-groups	1.166	7	.167	1.790	.127
Intra-groups	2.698	29	.093		
Total	3.863	36			

Table 6. ANOVA analysis of tensile strength with and without graphene

Tables 7 and 8 present the percentage elongation measurements and ANOVA analysis of the biofilms with and without graphene. It is observed that there are significant differences between the biofilms tested with a significance level of 0.002, Formulation 6*, which is composed of 20 g of orange peel, 40 g of pectin, 40 g of glycerin and 5 g of graphene, is the one that presented the highest percentage of elongation. In general, the With graphene biofilms presented the highest percentage of elongation.

Formulation	Elongation (%)	Standard deviation
1	12.62373	1.58475
2	15.34235	3.65145
3	16.38302	4.61498
4	13.86061	3.54382
5	14.53879	2.65886
6*	28.97739	7.64682
7*	19.16105	1.90648
8*	18.70799	10.7823

Table 7. Percentage of biofilm elongation with and without graphene

* With graphene

	Sum of squares	gl	Mean square	F	Sig.
Inter-groups	795.029	7	113.576	4.321	.002
Intra-groups	762.184	29	26.282		
Total	1557.213	36			

	Formulation	N	Subset for alpha = 0.05	
			1	2
HSD of Tukey[a,b]	1.00	5	12.6237	
	4.00	5	13.8606	
	5.00	5	14.5388	
	2.00	5	15.3424	
	3.00	5	16.3834	
	8.00*	4	18.7080	18.7080
	7.00*	4	19.1611	19.1611
	6.00*	4		28.9775
Duncan[a,b]	1.00	5	12.6237	
	4.00	5	13.8606	
	5.00	5	14.5388	
	2.00	5	15.3424	
	3.00	5	16.3834	
	8.00*	4	18.7080	
	7.00*	4	19.1611	
	6.00*	4		28.9775

Table 8. ANOVA analysis of the percentage of elongation with and without graphene

The means for the groups in the homogeneous subsets are shown.

a) Use the sample size of the harmonic mean = 4.571.

b) The sizes of the groups are not the same. The harmonic mean of the group sizes will be used. Type I error levels are not guaranteed.

Tables 9 and 10 present the Young's modulus measurements and ANOVA analysis of the biofilms with and without graphene, which indicates the level of resistance to deformation of the material. Formulation 6* shows the lowest Young's modulus which coincides with its characteristics since it has the highest percentage of elongation. Formulation 1 that does not contain graphene presented the highest Young's modulus, which is why it has among its characteristics greater tension than elongation, while among the formulations that contained graphene, Formulation 7* with 10 g of graphene presented the highest Young's modulus. in relation to formulations 6* and 8*, with a significance level of 0.003.

Formulation	Young's modulus	Standard deviation
1	0.114028914	0.01577061
2	0.071286836	0.01491216
3	0.06644655	0.01371027
4	0.08043416	0.00653398
5	0.098305021	0.01321596
6*	0.053357023	0.01422536
7*	0.077702752	0.00832045
8*	0.069668108	0.01904601

Table 9. Young's modulus in biofilms with and without graphene

* With graphene

	Sum of squares	gl	Mean square	F	Sig.
Inter-groups	.012	7	.002	4.053	.003
Intra-groups	.012	29	.000		
Total	.024	36			

	Formulation	N	Subset for alpha = 0.05	
			1	2
HSD of Tukey[a,b]	6.00*	4	.0534	
	2.00	5	.0555	
	3.00	5	.0663	
	8.00*	4	.0696	.0696
	5.00	5	.0776	.0776
	7.00*	4	.0777	.0777
	4.00	5	.0804	.0804
	1.00	5		.1140
Duncan[a,b]	6.00*	4	.0534	
	2.00	5	.0555	
	3.00	5	.0663	
	8.00*	4	.0696	
	5.00	5	.0776	
	7.00*	4	.0777	
	4.00	5	.0804	
	1.00	5		.1140

Table 10. ANOVA analysis of Young's modulus with and without graphene

The means for the groups in the homogeneous subsets are shown.

a) Use the sample size of the harmonic mean = 4.571.

b) The sizes of the groups are not the same. The harmonic mean of the group sizes will be used. Type I error levels are not guaranteed.

Table 11 and 12 show the vapor permeability data and ANOVA analysis in the biofilms with and without graphene, which measures the mass of water that passes through the biofilm in a given time. The ANOVA analysis shows with a significance level of 0.856 that there are no significant differences between the formulations.

Formulation	Water vapor permeability (g/h mm^2)	Standard deviation
1	0.01747459	0.00021454
2	0.01096537	0.00775369
3	0.01520809	0.00054449
4	0.01435188	0.02029662
5	0.02947766	0.0105062
6*	0.00950643	0.00672206
7*	0.01261861	0.00892271
8*	0.01357310	0.00057841

Table 11. Water vapor permeability in biofilms with and without graphene

* With graphene

	Sum of squares	gl	Mean square	F	Sig.
Inter-groups	.001	7	.000	.434	.856
Intra-groups	.001	8	.000		
Total	.002	15			

Table 12. ANOVA analysis of vapor permeability with and without graphene

Tables 13 and 14 present the results of water solubility and ANOVA analysis in biofilms with graphene and without graphene, which measures the proportion of biofilm that is soluble in water. According to the ANOVA analysis with a significance level of 0.778, there are no significant differences between biofilms with and without graphene.

Formulation	Solubility (%)	Standard deviation
1	0.23870266	0.169916366
2	0.12037319	0.085193496
3	0.1497932	0.041452403
4	0.21195541	0.207136363
5	0.12300524	0.089726159
6*	0.09025403	0.044302381
7*	0.05970151	5.04064E-05
8*	0.09152728	0.041050767

Table 13. Water solubility in biofilms with and without graphene

* With graphene

	Sum of squares	gl	Mean square	F	Sig.
Inter-groups	.074	7	.011	.549	.778
Intra-groups	.155	8	.019		
Total	.229	15			

Table 14. ANOVA analysis of the with and without graphene

In comparison with the mechanical properties reported (1; Beeva et al. 2015; Mujal-Rosas, 2010) for synthetic polymers used for packaging (Table 15), the biofilms obtained in this work could only be used as protection material for perishable products.

Polymer	Tensile strength (N/mm^2)	Young's modulus
PET	150	9
Polyethylene	30	1
Polyamide Nylon	40	2.9
Polystyrene	48	3.4
Polypropylene	27	1.3

Table 15. Propiedades mecánicas de los polímeros sintéticos

ECONOMIC ENGINEERING

Table 16 shows the average price in Mexican pesos of the raw material and Table 17 shows the cost of raw material to produce one kilogram of biopolymer. It is observed that the biopolymer where graphene is added in Formulation 6 and 7 increases the cost on average 116 times and in Formulation 7 it increases it on average 231 times more in relation to the formulations that do not contain graphene in their Formulation.

Raw material	Average price
Orange peel	110 $/Kg
Citrus pectin	600 $/Kg
Glycerin	145 $/Kg
Graphene	736,400 $/Kg

Table 16. Raw material price

Formulation	Average MP Cost ($ MNX/Kg)
1	271.0
2	295.5
3	320.0
4	344.5
5	369.0
6	37,140.0
7	73,960.0
8	37,140.0

Table 17. Raw material cost to produce one kilogram of biopolymer

Table 18 shows the variable and fixed costs to produce 1 kilogram of biopolymer in Mexican pesos for any of the formulations in one day of operation.

Concept	**Cost ($MNX/Kg)**
Variables costs	
Operation labor ($)	141.70
Supervision labor ($)	21.26
Auxiliary services	
Electric power ($)	0.05
Water ($)	0.014
Maintenance and repair ($)	1.56
Supply and operation ($)	10.87
Fixed costs	
Fixed operating cost ($)	65.18
Fixed investment cost ($)	72.50

Table 18. Costs to produce 1 kilogram of biopolymer

Table 19 shows the sales price of the different biopolymer formulations tested with a profit of 10% and Table 20 shows the sales price of the synthetic polymers.

Formulation	Sale price ($ MNX/Kg)
1	642.5
2	669.5
3	696.4
4	723.4
5	750.3
6	41,198.4
7	81,700.4
8	41,198.4

Table 19. Biopolymer price

Polymer	Sale price ($MNX/Kg)
PET	20.0
Polyethylene	22.5
Polyamide Nylon	62.5
Polypropylene	27.5
Polystyrene	27.5

Table 20. Price of synthetic polymers

It is observed that the sales price of biopolymers without and with graphene, respectively, is 12 and 1000 times higher than the sales price of synthetic polymers. Thus, the sale of biopolymers could be considered non-viable, however, it is also essential to consider the environmental impact of these materials based on the storage costs and degradation periods, which are expenses paid by the government from taxes. taxpayers so it generates an extra cost.

From the real cost that will consider the sales price and the cost of storage and treatment of synthetic plastics according to their degradation times reported in the literature (Table 21).

Polymer	Degradation time (years)	Real cost ($MNX/Kg)
PET	150	$14,667
Polyethylene	1000	$2,433,433,009
Polyamide Nylon	300	$20,302,119
Polypropylene	300	$20,302,084
Polystyrene	800	$1,000,068,054

Table 21. Real cost of synthetic polymers according to their degradation time

Table 22 shows the real cost based on considering the sales price and the cost of composting the biopolymer for a period of 5 years. We can observe that when considering the environmental impact expense generated by both synthetic polymers and biopolymers, the use of biopolymers is more viable since the costs that accumulate due to degradation times are lower in the case of biopolymers.

Formulation	Degradation time (years)	Real cost ($MNX/Kg)
1	5	$1,907.26
2	5	$1,934.26
3	5	$1,961.16
4	5	$1,988.16
5	5	$2,015.06
6	5	$42,463.16
7	5	$82,965.16
8	5	$42,463.16

Table 22. Real cost of biopolymers according to their degradation time

CONCLUSIONS

Plastics around the world represent a pollution problem, which is why it has been decided to produce biopolymers. This work aimed to study the mechanical and economic advantages of producing graphene-modified biopolymers. It was observed that properties such as: tensile strength, water vapor permeability and water solubility did not have significant differences with and without graphene, but not for elongation and Young's modulus, which showed improvements when adding graphene to its formulation. With respect to the economic part, it was determined that the production of biopolymers is much more expensive than synthetic polymers, however, when adding the cost that the disposal and storage of waste represents for the Government, biopolymers are more viable than synthetic polymers. synthetics, which denotes an opportunity cost not only for the environmental impact but also for the economic impact.

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