



Improvements of Thermoplastic Biodegradable Starch Polymer

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Abstract

This research aims to produce a biodegradable polymer from an available renewable source in a way that uses local agricultural waste as an additive. Also testing the properties of the polymer.

Starch was polymerized using tap water, three different acids were used (acetic acid, citric acid and fresh lemon juice). Glycerin was used as a plasticizer and olive waste as an additive. The polymerization process needed heat, a polymer sheet resulted after casting and cooling the polymer solution.

The effect of different acids, adding glycerin, replacing acetic with citric acid and the effect of adding olive waste on the mechanical and thermal properties of the polymer was tested using the tensile test machine and the differential scanning calorimetry (DSC). The biodegradability was tested by soaking the polymer in water until it decomposes forming septic and the digestive ability was tested on laboratory mice.

The acetic acid sample had the highest strength and modulus of elasticity among the three acids 6.30362, 287.454 MPa respectively and the lower ductility 3.42% this indicated a high crystallinity percentage which was proven using the DSC machine where its enthalpy of melting (ΔH) was the highest (135.3884 kJ/kg), thus it was chosen as a base for the enhancing. The acetic acid polymer's strength and elasticity increased by lowering the glycerin composition and so its crystallinity, where its ductility decreased. The opposite happened when gradually replacing the acetic acid with citric acid. The strength and elasticity decreased along with the increase in the ductility when olive waste was added but the crystallinity increased.

For the digestive test, the citric polymer started to be digested in the mice's stomach within one to one and a half an hour, the polymer also reached the intestines of the mice and got out of its system. All the polymer samples degraded within 7 days of soaking in water.



Introduction

The use of Synthetic, Non-biodegradable plastics and their environmental impact are already alarming, due to their inappropriate disposal and the requirement of a substantially longer time to degrade than the duration of their application, but one alternative could be the promising route of development and use of biodegradable polymers. [1, 2]

Biodegradable plastics and polymers were first introduced in 1980s. There are many sources of biodegradable plastics, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources.[3]

Polymers from renewable resources are receiving increasing attention as alternatives to non-biodegradable synthetic polymers. Among these, starch is the most widely produced renewable resource used in plastics [4]. Starch has a semicrystalline structure and is composed of two types of molecules: amylose, a linear polymer and amylopectine, a branched one. Starch from different sources like maize, rice and wheat have been used in the polymer industry for years as a solid filler for rubber and plastic [5, 6] The main purpose in that case is to reduce the cost, but its use is severely limited due to its poor mechanical performance, poor process ability and high water uptake levels. As an important application of starch is Thermoplastic starch polymer(TPS), starch granules can be gelatinized in the presence of a plasticizer (like water) and heat during which the crystalline structure is disrupted, to destroy the crystalline structure of starch and form a semi-crystalline thermoplastic starch. [7, 8]

The main disadvantages of TPS is the unsatisfactory mechanical properties. One problem is the fragile nature because of the molecular chain of starch. Moreover, the eventual migration of plasticizers into the environment increases the fragility of the material. This fragility is a structural stability problem, which increases with time because of the decrease in free volume and retrogradation [9] Various plasticizers were evaluated to improve the processing properties and product performance of TPS blends e.g. glycerol, urea, formamide, sorbitol, citric acid, glycol, and amino acids.[10]

Preparing the polymer in this research was done in three steps, the first step was mixing the ingredients; the starch was added to water at room temperature and mixed until a homogenous solution formed, after all the starch had been dissolved; the acid and the plasticizer (if used) were added directly and mixed. The second step was mixing the polymer components using a heater at an approximated temperature of 80 °C. The third step was casting the mixture over a surface and let it cool overnight. For the olive waste samples, the olive waste weight was taken from the starch's, so it's 2.5% and 10% from the starch weight. Mechanical, thermal and biodegradability properties were tested along with the digestive capability.

Experimental Work

I. Materials

The thermoplastic polymer blend consists of four primary elements; starch, water, plasticizer and acid. Each of these elements composition has its effect on the properties of the product. All materials used in this project were supplied from the local market, they were:

1. Corn starch
2. Plasticizer: glycerin
3. Acids: citric acid, acetic acid and fresh lemon juice
4. Water
5. Agricultural waste as additive: olive waste.

II. Sample preparation



The methodology used in preparing the polymer was 4 steps; the first step was mixing the ingredients; the starch were added to water at room temperature and mixed until a homogenous solution formed, after all the starch had been dissolved 10g of 15% acid and the plasticizer (if used) were added directly and mixed. The second step was mixing the polymer components using a heater at an approximated temperature of 80 °C. The third step was casting the mixture over a surface and let it cool overnight. For the olive waste samples, the olive waste weight was taken from the starch's, so it's 2.5% and 10% from the starch weight. All prepared samples are shown in Table (1).

Table 1: Thermoplastic Starch Polymer Samples.

component samples	Acid	Starch (g)	Water (g)	plasticizer	Glycerin (g)	%Olive waste of starch
A1	Acetic acid	9.50	63.80	High glycerin	3.16	0.00%
A2	Acetic acid	9.50	65.30	Low glycerin	1.60	0.00%
A3	Acetic acid	9.50	66.80	No glycerin	0.00	0.00%
C1	Citric acid	9.50	63.80	High glycerin	3.16	0.00%
C2	Citric acid	9.50	65.30	Low glycerin	1.60	0.00%
C3	Citric acid	9.50	66.80	No glycerin	0.00	0.00%
L1	Lemon juice	9.50	65.30	Low glycerin	1.60	0.00%
L2	Lemon juice	9.50	66.80	No glycerin	0.00	0.00%
2/3A-1/3C	Acetic & citric	9.50	63.80	High glycerin	3.16	0.00%
1/2A-1/2C	Acetic & citric	9.50	63.80	High glycerin	3.16	0.00%
1/3A-2/3C	Acetic & citric	9.50	63.80	High glycerin	3.16	0.00%
OWL	Acetic acid	7.125	63.80	High glycerin	3.16	2.50%
OWH	Acetic acid	8.55	63.80	high glycerin	3.16	10.00%

III. Testing

1. Tensile test

Tensile test was carried out by using Sinwon Test Machine ST Series at constant speed 5mm/min and at room temperature. For each sample, three specimens were tested. The samples were 45 to 50 mm gauge length, Tensile Test provides values of the tensile strength, modulus of elasticity by 1% strain secant method and ductility as percent elongation at break.

2. Differential Scanning Calorimeter (DSC)

The thermal properties of some prepared samples were evaluated using a differential scanning calorimeter (DSC) model Pyrix-6, Perk in Elmer, Corporation, U.K. 4.3 to 5.4 mg samples, encapsulated in a hermetically sealed aluminum pan, were prepared. The same temperature profile was applied to all samples. Samples were heated at 10°C/min. The thermal transition such as fusion was scanned in a temperature profile of 20-230°C. Melting temperature and heat of fusion of the samples were obtained from the maximum peak and area under the peak respectively, where the last is essential in estimating the percentage of crystalline regions.

3. Digestion capability

Five laboratories mice were used in testing the digestion capability of the C3 sample, since it was expected to be non-toxic to the mice. The mice were inoculated orally with powdered dyed polymer mixed with water. The stomach and intestines of the mouse was tested using a 2000× microscope magnification to track the polymer traces. Each mouse was tested within a period of half-an-hour, the test took 2 and half an hour to test all five mice.

4. Biodegradability

A 0.1 g of samples from 1 to 7 was soak in water for several days until they decomposed.



Results

1- Mechanical and thermal properties testing

From the tensile test the strength, modulus of elasticity and ductility were calculated, the thermal properties (enthalpy of melting and the melting temperature) was obtained from the DSC diagram, the results were as follow:

A- Acid effect on polymer

The effect of acid type on mechanical and thermal properties of starch polymer is shown in Table (2)

Table 2: Acid Effect on Starch Polymer.

	Strength (MPa)	Modulus (MPa)	ductility	Enthalpy of melting (kJ/kg)	Tm (°C)
(A1)	6.30	287.45	3.42	135.00	76.76
(L1)	3.31	133.51	21.78	-----	
(C1)	1.33	16.70	65.15	127.87	94.61

The acetic sample had the highest strength and modulus of elasticity but the lowest ductility which was approved by the DSC results, where the enthalpy of melting of acetic sample was the highest, that was the reason why the acetic acid was chosen as a base for the other tests.

B- Glycerin effect on Acetic acid sample and Citric acid samples

The effect of glycerin as a plasticizer was studied and results are shown in Table (3)

Table 3: Glycerin Effect on Acetic Acid and Citric Acid.

	Strength (MPa)	Modulus (MPa)	ductility	Enthalpy of melting (kJ/kg)	Tm (°C)
A1	6.30	287.45	3.42	135.00	76.76
A2	6.83	392.25	1.89	175.80	85.62
C1	1.33	16.70	65.15	127.87	94.61
C2	4.96	328.00	1.90	-----	-----

From this table it is clear that glycerin weaken the mechanical properties of the samples and also decrease the crystallinity.

C- Replacing Acetic Acid with Citric acid effect

The effect of percentage of citric acid (replacing Acetic acid) on mechanical properties was studied and the results are shown in Table (4)

Table 4: Replacing Acetic Acid with Citric Acid Effect.

	Strength (MPa)	Modulus (MPa)	Ductility	Enthalpy of melting (kJ/kg)	Tm (°C)
A1	6.30	287.45	3.42	135.00	76.76
2/3A-1/3C	1.34	16.98	66.26	-----	-----
1/2A-1/2C	1.01	8.23	73.13	63.34	84.79
1/3A-2/3C	1.15	14.55	67.31	77.46	90.49
C1	1.33	16.70	65.15	127.87	94.61

Replacing the acetic acid with citric acid decreased the strength and the modulus of elasticity but increased the ductility, it also decreased the crystallinity, when the citric composition overcame the



acetic composition the strength, modulus of elasticity and the crystallinity increased but didn't reach the pure acetic sample properties.

D- Olive solid waste effect on acetic acid polymer

Olive solid waste as a natural additive was added to starch polymer to observe its effect on both mechanical and thermal properties, results are shown in Table (5)

Table 5: Olive Effect on Acetic Acid Polymer.

	Strength (MPa)	Modulus (MPa)	ductility	Enthalpy of melting (kJ/kg)	Tm (°C)
A1	6.30	287.45	3.42	135.00	76.76
OWL	1.95	99.56	24.05	-----	-----
OWH	1.62	58.08	31.52	168.57	82.60

As the percentage of olive waste increased the strength and modulus decreased but the ductility increased. For the crystallinity, it increased as the olive waste percentage increased.

2- Digestion capability test

At first the polymer was crushed to form a powder then mixed with water, the powdered polymer mixed with water is shown in Figure (1):



Figure 1: Powdered Dyed C3 Sample Mixed with Water.

First the polymer was tested under the microscope by itself to compare it with the polymer after fed to mice, the micrograph is shown in Figure (2).



Figure 2: C3 Sample under the Microscope.



Different samples were taken from the stomach and intestines at half of an hour periods. At first the dye separated from the polymer as shown in the following figure, Figure (3)

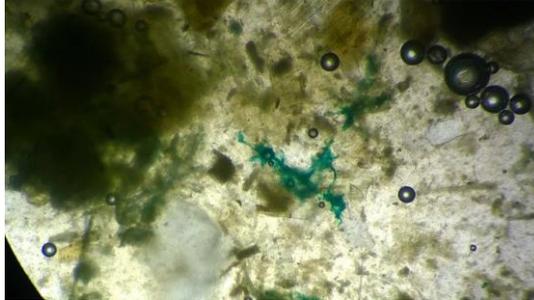


Figure 3: The Separation of the Dye from the Polymer.

After almost an hour the polymer started to get digested in the stomach which is clear from the edges of the polymer pieces, Figure (4)

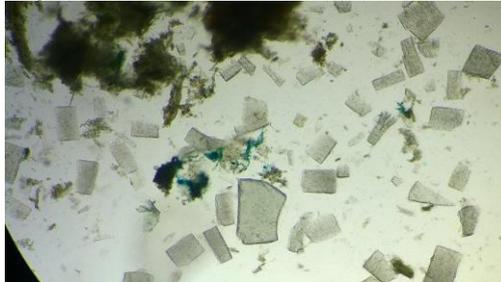


Figure 4: The Digested Polymer in the Stomach.

The digested polymer in the intestines of the mouse, where it became almost transparent and with digested edges.

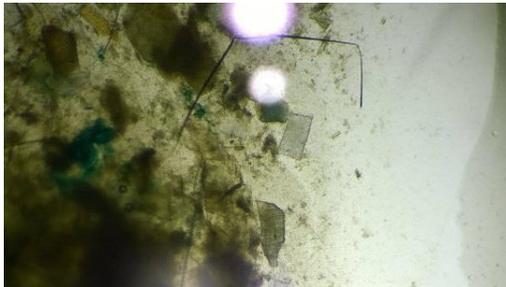


Figure 5: The Digested Polymer in the Intestines of the Mice.

Biodegradability of the polymer

The 7 samples that were soaked in water after 4 days as shown in Figure (6):



Figure 6: Samples After 4 days of Soaking in Water.

The first two from the left were acetic acid samples with high and low glycerin (they didn't degrade yet), the second three were citric acid samples and the final two were lemon samples.



The first and fourth sample had high glycerin contents, followed by the second and fifth samples, the rest had no glycerin in their compositions.

Discussion

1. Mechanical and thermal properties

i. Acid effect on the polymer

The effect of different acids (acetic (A), Lemon (L) and Citric (C)) on tensile strength and modulus of elasticity of prepared starch polymers is shown on Figure (7)

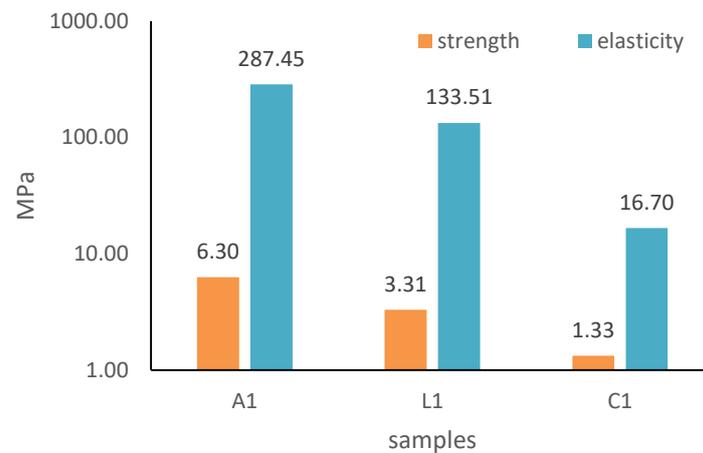


Figure 7: Acid Effect on the Strength and Modulus of Elasticity of the Polymer.

It's clear from Figure (7) that the acetic acid has the highest strength and modulus followed by the lemon and finally the citric, the opposite happens with the ductility as shown Figure (13), where the citric sample has the highest ductility followed by the lemon samples and finally the acetic samples. This is a normal relation between the strength and ductility.

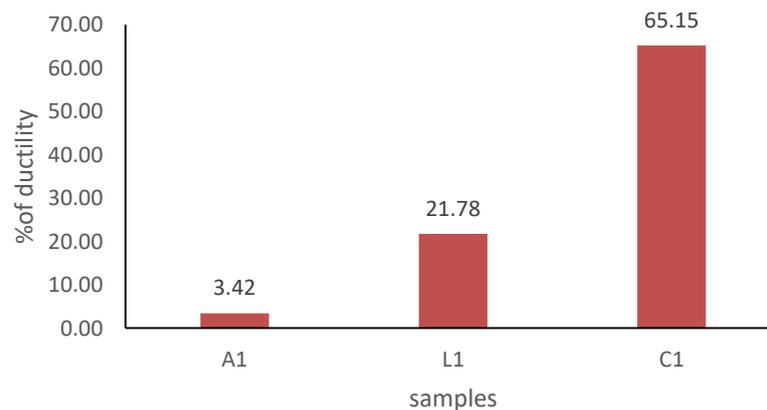


Figure 8: Acid Effect on Ductility (%EL).

The citric acid's melting temperature is higher than the melting temperature of the acetic, 76.76 and 94.61 respectively as shown in table 2, despite the fact that the acetic acid has higher crystallinity with 135 kJ/kg melting enthalpy than the crystallinity of citric sample with 127.87 kJ/kg melting enthalpy, this might be due to cross-linked regions that are formed because of the citric acid this was proven by N.Reddy and Y.Young when they used citric acid as -crosslinking agent. [11]

ii. Glycerin effect on the polymer



The effect of glycerin on both acetic and citric samples was studied and the results regarding mechanical properties (Tensile strength and Modulus of elasticity) are shown in Figure (9).

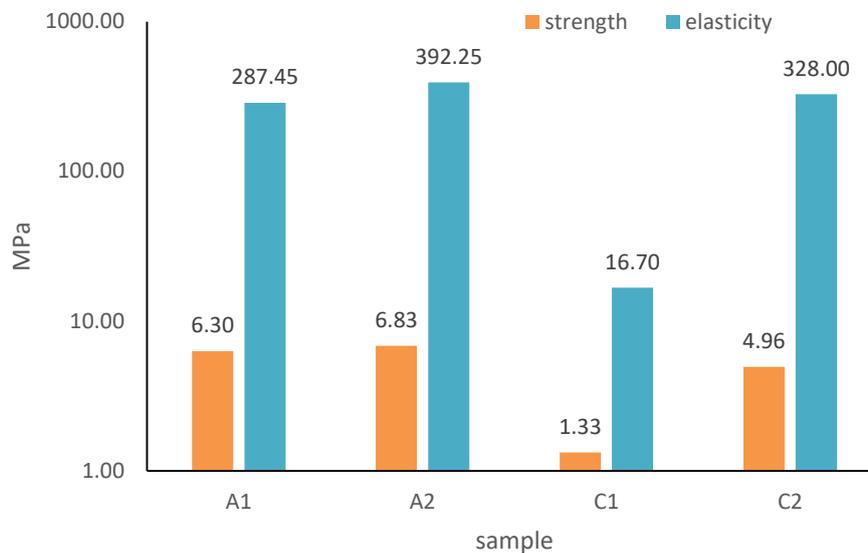


Figure 9: Glycerin Effect on the Strength and Modulus of Elasticity of the Polymer.

Increasing the glycerin decreases the strength and modulus of elasticity as Figure 14 shows, this might be due to the decrease in crystallinity. This effect can be justified by knowing the effect of adding glycerin to the TPS as a plasticizer, which involves the introduction of side chains that reduce the intermolecular forces between the polymer molecules themselves and causes a decrease in crystallinity and melting temperature. As E. H. IMMERGUT and H. F. MARK proved in their paper. [12]

Glycerin has larger effect on the citric samples more than the acetic samples, since plasticizer molecule will have much more difficulty in penetrating the crystalline regions, where there is a minimum of free space between the polymer chains than the amorphous regions; the acetic sample is more crystalline with an enthalpy of melting equals to 135 kJ/kg which is higher than the citric sample with 127.87 kJ/kg enthalpy of melting. Crystallinity should, therefore, be considered as a factor opposing plasticization. [13].

As the crystallinity increases the ductility decreases as shown in the Figure (10)

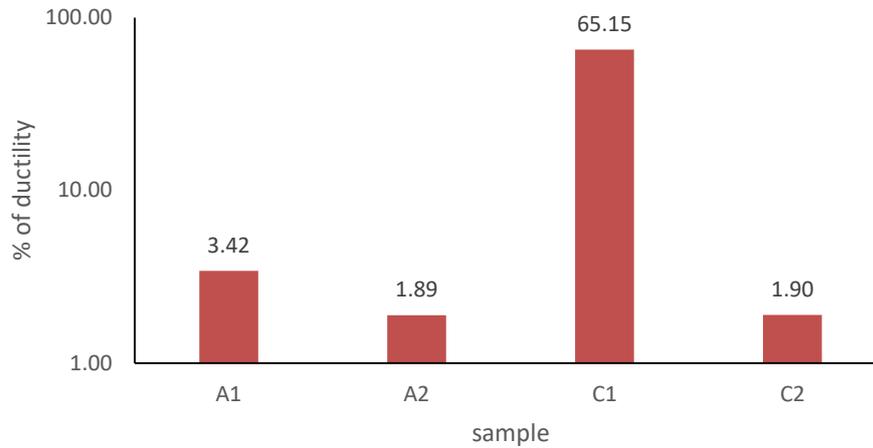


Figure 10: Glycerin Effect on the Polymer's Ductility

iii. Replacing the acetic acid with citric acid

Acetic acid was replaced partially by citric acid to study the effect of this combination on mechanical and thermal properties; results for strength and modulus are shown in Figure (11)

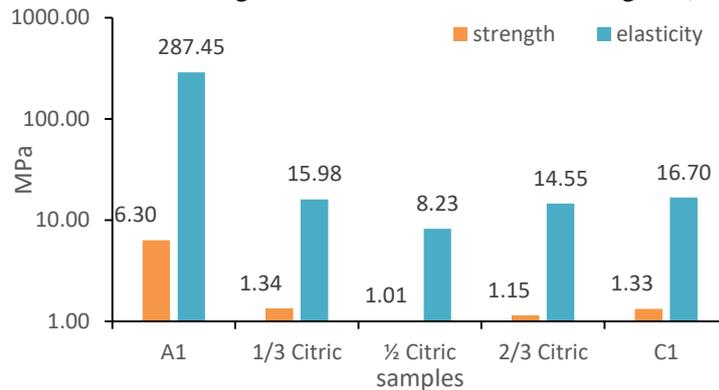


Figure 11: Replacing Acetic with Citric Effect on the Polymer.

when adding citric to acetic the randomness increases and so the crystallinity decreases, this is why the half-acetic half-citric sample has the lowest melting enthalpy, strength and elasticity as shown in figure (11), but the highest ductility as shown in Figure (12). When the citric composition start to overcome the acetic composition the crystallinity went up again, but not as when the acetic composition is higher than the citric, this is due to the higher crystallinity in pure acetic sample with 135 kJ/kg melting enthalpy than pure citric sample with 127.87 kJ/kg melting enthalpy.

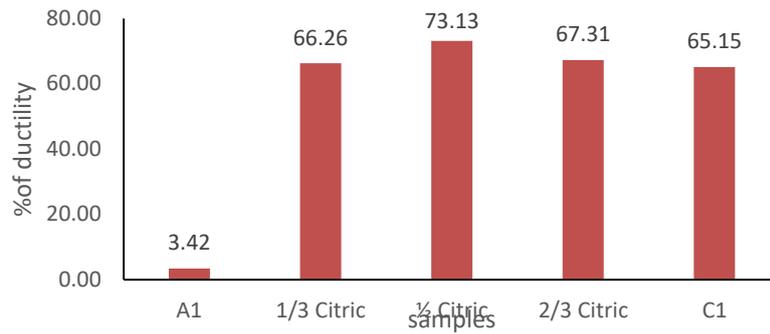


Figure 12: Citric Acid Effect on the Polymer's Ductility

iv. Olive waste effect

Olive solid waste was selected as a natural waste to be added to starch polymer to observe its effect on properties as shown in Figures (13) and (14)

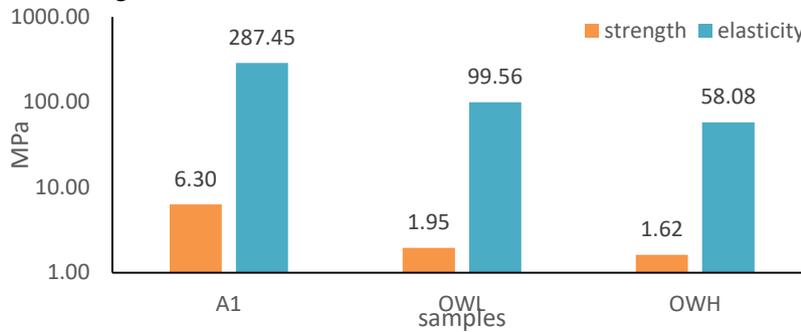


Figure 13: Olive Waste Effect on the Polymer's Strength and Elasticity.

As shown in Figure (11) Tensile strength and modulus of elasticity decrease with increasing olive solid waste percentage and that might be due to formed of the voids that resulted from the poor compatibility between the polymer and the olive waste have, as for the ductility it should decrease because of the voids but apparently it behaves oppositely as shown in Figure (12), the reason is that the olive waste wasn't fully-dried and had small percentage of oil, and the oil could act as a plasticizer.

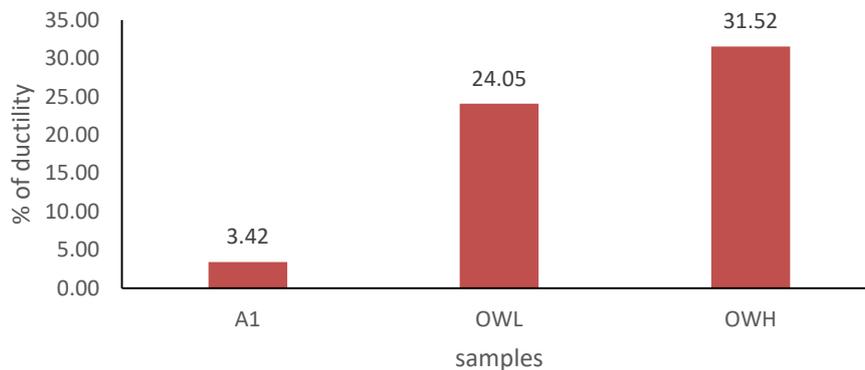


Figure 14: Olive Waste Effect on the Ductility of the Polymer.

Table (5) shows an increase in crystallinity where the enthalpy of melting jumped from 135 to 168.57 kJ/kg, this contradicts with the strength and the elasticity results, this can be justified by assuming some cross-linking occurred due to an addition of olive solid waste which may contain some active



materials such as metallic polymeric compounds (polymerin), a study done by BOLAÑOS, JUAN FERNÁNDEZ-, ET AL proved the effect of polymerin on crystallinity and cross-linking [14].

2. Digestion Capability

The citric acid with no glycerin sample (C3) is used for testing the digestive capability for two reasons; first for the expectations of no toxicity from the citric acid, also glycerin might cause some intestines problems for the mice. The polymer didn't form a solution with the water but a mixture as shown in figure 2, the reason why is because starch polymer doesn't dissolve in water under the normal conditions. The dye separated from the polymer because of the incompatibility between the polymer and the dye as shown in figure 3. As for the short periods of half an hour it's because of the small digestive system the mice have, that gets rid of what's in the mice's digestive system within 2 to 2:30 hours.

The polymer starts to digest in the mice's stomach after almost 1 hour which is shown in figure 3, when the edges of the polymer starts to get less sharper than they normally were in figure 2, also the digestion doesn't stop in the stomach, more polymer is digested in the intestines of the mice as shown in figure 4. This is a proof of the digestive capability of the polymer for both humans and animals.

3. Biodegradability

The samples that has no glycerin in their composition decompose within the first 3 days of soaking, the lemon sample with glycerin degrades faster than the citric sample, where it took the lemon with glycerin sample 4 days to degrade and the citric 5 days. The slowest one to degrade was the acetic samples (high and low glycerin composition), they took almost 7 days to start degradation.

The lemon juice has high citric acid in its components along with the ascorbic acid and malic acid according to the Modern Gastronomy: A to Z book [15] that's why the lemon juice samples has closer degradation properties to the citric acid samples. The reason why it takes the acetic acid more time to degrade might be due to higher crystallinity, thus stronger bonds between the polymer molecules that the bacteria can't easily penetrate and decompose.

Conclusion

It was observed that the Strength and modulus of elasticity are directly proportional to the crystallinity in case of no other disturbances, and inversely proportional with the percentage of ductility. Therefore, Increasing the randomness in the polymer definitely will decrease the crystallinity. The acetic acid samples gives higher crystallinity to the polymer than the lemon juice and the citric acid, hence, the lemon juice and the citric acid produced more randomness in the polymer. Citric acid forms cross-linking in the polymer.

It was concluded that glycerin acts as a crystallinity opposing agent, it also gives the polymer higher ductility, but it lowers the strength and modulus of elasticity.

On another hand, olive waste creates voids in the polymer, thus it lowers the strength and modulus of elasticity. However, it contains polymerin which enhance the crystallinity in the polymer and the olive oil residue in the olive waste may act as a plasticizer.

Finally, it was clear that the starch polymer can be digested and it cause no harm to the digestive system. Moreover, the starch polymer is a biodegradable polymer, therefore, thermoplastic starch polymer is an environmental friendly polymer.

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