STUDY OF THE EFFICIENCY OF THE USES OF POLYVINYL ALCOHOL AND GLYCEROL AS PLASTIFIERS IN POLYMERIC BLENDS CONTAINING PBAT AND STARCH

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Abstract: The biodegradable polymer PBAT can form blends with natural and abundant polymers such as starch, resulting in materials suitable to produce packaging that has a reduced environmental impact upon disposal. PVOH and glycerol have shown promise as plasticizers in these blends, improving their mechanical properties and degradation rates. In the present study, through extrusion processes, injection molding, tensile mechanical and impact tests, PBAT/starch polymer blends plasticized separately with PVOH, and glycerol were produced and evaluated. The obtained data support the plasticizing capabilities of PVOH and glycerol, reducing the tensile modulus of the blends by 21 and 54%, respectively.

Keywords: Biopolymers; thermoplastic starch; Polyvinyl Alcohol; Plasticizer.

ESTUDO DA EFICIÊNCIA DOS USOS DE ÁLCOOL POLIVINÍLICO E DE GLICEROL COMO PLASTIFICANTES EM BLENDAS POLIMÉRICAS DE PBAT E AMIDO

Resumo: O polímero biodegradável PBAT tem a capacidade de compor blendas com polímeros naturais e abundantes como o amido, formando materiais aplicáveis na produção de embalagens cujo descarte impacte menos o meio ambiente. O PVOH e o glicerol têm se mostrado promissores como plastificantes nessas blendas, melhorando suas propriedades mecânicas e suas taxas de degradação. No atual estudo, através de processos de extrusão, injeção, ensaios mecânicos de tração e impacto, blendas poliméricas de PBAT/amido plastificadas separadamente por PVOH e glicerol foram produzidas e tiveram suas propriedades aferidas. Os dados obtidos respaldam as capacidades do PVOH e do glicerol de plastificarem as blendas, diminuindo seu módulo de elasticidade em 21 e 54%, respectivamente.

Palavras-chave: Biopolímeros; Amido termoplástico; Álcool Polivinílico; Plastificante.

1. INTRODUCTION

Over the past few decades, the uncontrolled use of fossil-based polymers has caused serious pollution problems to the planet. Some of these materials, such as polyethylene, polypropylene, and polystyrene, are widely used in the production of packaging for products. Considering that the production of such items cannot be halted, it is necessary to change their composition to minimize the environmental impact of their disposal [1].

Naturally occurring polymers such as starch, cellulose, and chitin, for example, due to their renewable nature, become interesting alternatives to non-biodegradable polymers. Additionally, these materials are agricultural waste, which makes them cost-effective and readily available. Starch, in particular, can be converted into thermoplastic materials by incorporating plasticizers such as polyvinyl alcohol, glycerol, sorbitol, among others. However, thermoplastic starch exhibits low mechanical strength, necessitating the addition of other preferably biodegradable polymers to enhance its physical properties. Several studies have reported satisfactory results using materials such as polylactic acid, polybutylene succinate, and polycaprolactone in creating blends with starch. These studies have found that these produced blends exhibited increased mechanical strength and water resistance compared to pure thermoplastic starch [2].

Polybutylene adipate terephthalate (PBAT) is a polymer that has attracted attention due to its processing conditions and mechanical properties similar to low-density polyethylene, as well as its environmentally friendly characteristics. PBAT blends with starch have been extensively studied due to the high performance and low cost of these composites. However, hydrophobic PBAT and hydrophilic starch exhibit low compatibility, requiring the addition of substances such as citric acid and maleic anhydride to act as compatibilizing agents. In studies involving thermoplastic starch/polyester blends produced via extrusion processes, for example, citric acid has shown better results as a compatibilizer than maleic anhydride, promoting crosslinking that increases the interaction between the polymer phases [3,4].

Polyvinyl alcohol (PVOH) and glycerol have shown promise as plasticizers in biodegradable polymer blends, as they can improve their mechanical properties and accelerate the degradation rate of these materials [5,6].

PVOH is a water-soluble polymer that can be used in applications requiring high solubility and biodegradability. In terms of packaging production, it shows promise due to its excellent oxygen barrier properties, high mechanical and chemical resistance, adhesion capacity, flexibility, and water solubility. When used in blends with other polymers, it can accelerate the degradation process of these materials. Starch, in particular, due to its large number of hydroxyl groups in its structure, can form hydrogen bonds with PVOH, ensuring satisfactory compatibility between these two components [2,3,5].

Glycerol is another organic compound that can be used in blends with thermoplastic starch to improve its mechanical properties and increase its biodegradability. Additionally, being a byproduct of the biofuel industry, it can be a sustainable and environmentally friendly alternative to produce biodegradable materials [6].

Therefore, the aim of this study is to evaluate the effectiveness of PVOH and glycerol as plasticizers in polymeric blends containing PBAT and starch. To this end, different formulations of polymeric blends were produced, and their mechanical properties were subsequently evaluated through tensile and impact tests.

2. METHODOLOGY

The PBAT Ecoflex® polymer was supplied by BASF, and the cassava starch filler was provided by Podium Alimentos. As for the plasticizers used, glycerol and PVOH were produced by Neon. Glycerol has a purity of 99.9%, and PVOH has a degree of hydrolysis of 87.57%. The anhydrous citric acid additive used was manufactured by Tate & Lyle.

The methodology of the current study involved drying, extrusion, dehumidification processes to produce test specimens through injection molding, followed by subsequent characterization.

After drying the PBAT and starch in an oven at 90°C for approximately 48 hours, the material was processed using a co-rotating twin-screw extruder, Imacom DRC 30:40 IF model, with a screw diameter of 30 mm and an L/D ratio of 40. The material was extruded with the following temperature profile configured for the extruder: 80, 90, 95, 100, 110, 120, 130, 140, 150, 160, and 60°C. Additionally, the screw speed was set to 45 RPM.

The compositions of the produced formulations in percentage can be seen in Table 1.

Table 1. Composition of the blends produced via extrusion process.

	PBAT	Starch	Glycerol	PVOH	Citric acid
F0	100%	-	-	-	-
F1	60%	40%	-	-	-

F2	60%	27%	12%	-	1%
F3	60%	27%	-	12%	1%

Source: Author’s own.

To obtain the test specimens, a ROMI injection molding machine, Primax model, with a closing force capacity of 100 tons, a 50 mm diameter universal screw, and an L/D ratio of 20 was used. Prior to injection, the material was dehumidified at 90°C using a PIOVAN dehumidifier, T501X model, for a minimum period of 6 hours. Furthermore, F0 and F1 did not show the addition of citric acid in their formulation, since its crosslinking increases the interaction between the starch and the polymer and improves the compatibilization of the formulations with the plasticizers [3].

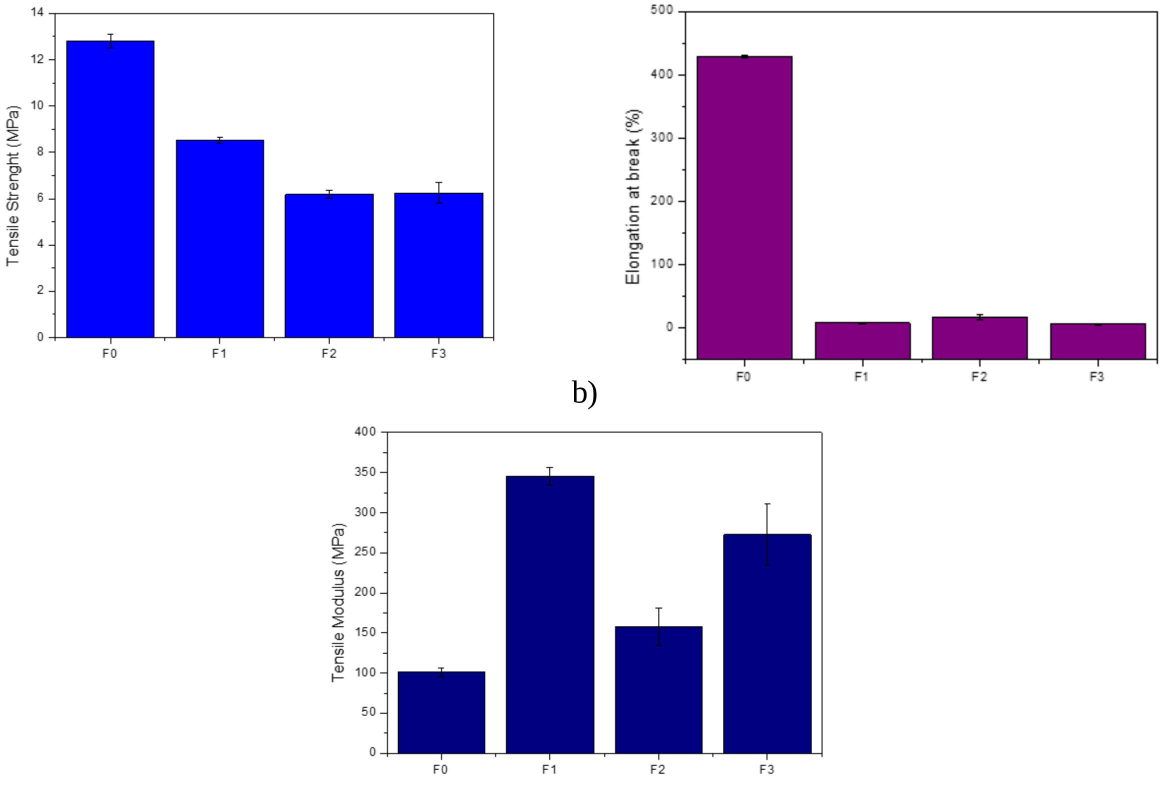
To evaluate the mechanical properties of the different blends, tensile tests were performed on their respective test specimens. The tests were conducted using an EMIC testing machine, DL 2000 model, following ISO 527 type 5 standard, without the use of an extensometer. A 9 KN load cell was used. The properties evaluated were maximum tensile strength, elastic modulus, and deformation at maximum force, at a displacement rate of 50 mm/min. Impact tests were carried out in accordance with ISO 180 on an EMIC brand machine using the Izod method with a 2 mm notch, in which one of the ends of the specimen is clamped during the test. No other characterization tests were performed in addition to the mechanical test.

3. RESULTS AND DISCUSSION

From the results obtained through uniaxial tensile tests, it was possible to analyze three main mechanical properties of the formulations: tensile strength, elongation at break and tensile modulus. Formulation F0 was the only one that did not break, which corroborates its visibly higher tensile strength (about 400%) compared to the others, as shown in Figure 1a. Additionally, regarding the values of elongation at break, displayed in Figure 1b, formulations F2 and F3 exhibited similar properties, despite variations in elasticity.

As seen in Figure 1c, tensile modulus of formulation F1 was the highest (approximately 350 MPa). This result confirms the study [3], which demonstrated that adding starch to the polymer matrix provides greater stiffness through the formation of crystalline networks. On the other hand, the addition of plasticizing agents, as observed by [2], decreased the rigidity of the composites.

Figure 1. Recorded values of (a) tensile strength; (b) elongation at break; (c) tensile modulus.



a)

b)

c)

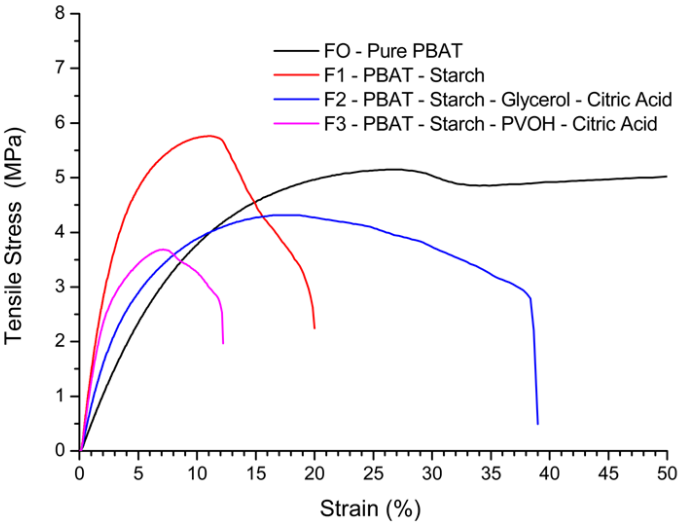
Source: Author's own.

The ability of formulation F0 to resist rupture, along with its higher tensile strength compared to the other formulations, suggests that glycerol and PVOH confer lower mechanical strength to the material compared to the control formulation. Additionally, formulations F2 and F3 demonstrate similar properties regarding elongation at break. However, the stiffness provided by PVOH was higher than that provided by glycerol, as indicated by the tensile modulus. This highlights a better contribution of glycerol to the plasticity of the blend.

Since PVOH is water-soluble, its compatibility with starch was only partially effective. Consequently, it was observed that some PVOH particles did not fully dissolve in the mixture, which could be explained by the incomplete dissolution of the plasticizer during the formulation preparation [5].

Figure 2 shows the stress-strain curves of the test specimens from the formulations during the tensile tests. As expected, formulation F0, being composed purely of polymer, had the highest elongation among the compared formulations, without specimen rupture. F1, despite not elongating significantly, had the highest stress peak among the test specimens, which can be attributed to the presence of starch as a filler, reinforcing the polymer matrices through hydrogen bonding with the polymer chains, making the material stiffer and less flexible [3]. As for the formulations containing plasticizer, it can be observed that F3 provided the lowest values for both variables, indicating that the addition of PVOH made the material less flexible compared to the addition of glycerol, resulting in greater deformation.

Figure 2. Tensile stress versus strain values of the formulations.

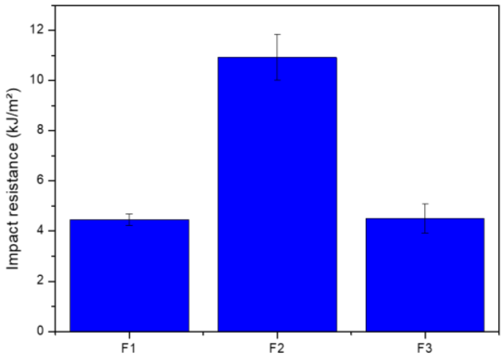


Source: Author's own.

The same impact testing methodology was implemented for the four formulations, with F0 being the only one that did not rupture during the tests. F1, containing only the polymer matrix and filler, was shown to be the stiffest of the formulations, absorbing less energy during impact and rupturing more easily. On the other hand, F2 achieved satisfactory results, with most samples rupturing only upon the return of the pendulum, highlighting the potential of glycerol as a plasticizer. Due to its ability to reduce the stiffness of the polymer material, glycerol increases its flexibility, leading to higher impact resistance and greater energy absorption during deformation. As a result, polymer blends containing glycerol as a plasticizer tend to exhibit higher toughness and resistance to failures under impact loads [7].

As for the PVOH present in F3, it did not cause a considerable increase in energy absorption compared to F1. Nevertheless, most test specimens ruptured only upon the return of the pendulum, similar to F2 samples. Thus, although PVOH has the capacity to decrease the stiffness of polymer blends, it did not prove to be effective in enhancing impact resistance when compared to glycerol. The obtained data are shown in Figure 3.

Figure 3. Impact resistance of formulations



Source: Author’s own.

4. CONCLUSION

The analyses support the potential of PVOH as a plasticizer, capable of improving the flexibility of materials and decreasing their modulus of elasticity by 21%. Additional studies can be done to further explore the properties of PVOH as a plasticizer and its applicability in the manufacture of packaging for products. No other characterization tests were performed in addition to the mechanical test.

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