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Revalorisation of a residue from the maize-snack industry through the development of bio-based materials. Effect of the plasticiser

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ABSTRACT

The current reliance on traditional plastics necessitates exploring natural-based alternatives derived from industrial by-products and waste. This study focuses on Nejayote, a waste product from the maize-snack industry, assessing its potential as a raw material. Glycerol and water (Gly and H_2O) were employed as plasticisers in injection-moulded nejayote-based bioplastics, and their evaluation through rheological, tensile, water uptake, and SEM microscopy tests. Higher H_2O ratios resulted in more easily processable blends with reduced consistency (η^* decreased from $(6.2 \pm 0.2)\cdot10^5$ to $(1.2 \pm 0.5)\cdot10^4$ Pa s). However, the formulation with the highest H_2O content exhibited increased consistency ($\eta^* = (5.3 \pm 0.3)\cdot10^7$ Pa s), since glycerol enhanced biopolymer chain mobility. Intermediate plasticiser combinations demonstrated a water uptake capacity of ~75%, making these bioplastics versatile for various applications. This research highlights the potential of utilising "Nejayote" and optimising formulation for sustainable bioplastic development.

1. Introduction

Natural biopolymers such as silk, wool, cotton, cellulose, proteins, starch, or natural rubber have been used since ancient times to manufacture objects with various applications (Bhatia, 2016). Common synthetic plastics are a stable, versatile, and durable materials with properties such as corrosion resistance, light weight, transparency, flexibility and durability. These properties make them of great interest in various sectors (Mann et al., 2020). Their production continues to grow rapidly, with almost 58 Mt produced in Europe (Pan et al., 2020). According to a recent report by the Organisation for Economic Cooperation and Development (OECD), global plastic consumption will reach 1231 Mt in 2060 (OECD, 2022). Keep in mind that not all plastics can be recycled, and if they can, they are only recycled once or twice, and many are incinerated or dumped of in landfills. This accumulation of waste kills wildlife and damages natural ecosystems (Agnihotri et al., 2020; de Souza Machado et al., 2018), and according to UN data, by 2050 there will be more plastic than fish in the oceans (de Jong, 2018). This requires the development of materials that allow society to continue to benefit from the usefulness of plastics, without the undesirable effects that occur after their disposal and generate environmental impacts. Therefore, it is convenient to link their production to the use of renewable natural resources, allowing their ultimate biodegradation and thus avoiding their accumulation in the environment (Lambert and Wagner, 2017; Li et al., 2022). For this reason, there is a continuing interest in the research community to find different bio-based alternatives to common plastics, for which waste streams from the food industry have attracted much attention (Kakadellis and Harris, 2020; Zhang et al., 2019).

Maize is the most widely grown cereal in the world. More specifically, the United States Department of Agriculture (USDA) estimates that global maize production will be around 1200 Mt in 2022/2023 (Brooks and Blandford, 2017). Maize has great genetic variability, with the main varieties being white, yellow, sweet, popcorn, blue, waxy, and high protein, each with unique characteristics. This grain is present in a wide range of consumer products and is the staple food of large population in Americas, Africa, and Asia (García-Lara and Serna-Saldivar, 2019). Industrially, maize is subjected to a process of wet milling, dry milling or nixtamalisation to obtain different products. In dry milling, starch and refined products are obtained, which are used in the production of snacks, cereals, syrups, and blond beer. Wet milling also produces pure starch, protein, fibre, and germ. Finally, nixtamalisation produces dry dough flours, tortillas, and appetizers (Serna-Saldivar and Chuck-Hernandez, 2019).

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Nixtamalisation is an alkaline cooking process that basically involves cooking maize in water with calcium hydroxide and can be described as a leaching process that causes the starch in the cereal to gel. The result of this process is the nixtamal, which is the grain that is transformed into processed products. Apart from the nixtamal, the "nejayote", or residual water is the waste that contains a high amount of organic solids as well as other solubilized ingredients (Castro-Muñoz et al., 2019). This waste is considered highly polluting because it contains high concentrations of suspended and dissolved organic matter, resulting in a high chemical oxygen demand. In addition, at the end of the process it is released at a high temperature (60–80 °C) and the pH is between 10 and 14 (non--suitable for living specie) (Argun and Argun, 2018). Consequently, this waste has dramatic consequences for the environment such as the death of fish and other aquatic life due to lack of oxygen, or it prevents the growth of plants because it changes the pH of the soil (Díaz-Montes et al., 2016). Some studies aim to use the solid fraction of the "nejayote" for animal feeding (Argun and Argun, 2018). Carvajal-Millán et al. (2005) patented the process for obtaining corn gum, showing its potential as a texturising agent for use implementation in the confectionery industry, given its structural properties in the food industry. In addition, certain components of the residue can act as stabilizing agents, providing viscosity, texture, and structure to bakery products (Chamorro and Mamani, 2010). Nejayote is also a source of antioxidants and dietary fibre, and its use is developing in the pharmaceutical industry due to the link between antioxidants and chronic diseases (Niño-Medina et al., 2010), as well as its anti-inflammatory activity (Buitimea-Cantúa et al., 2020). In the medical industry, we can highlight their involvement as immunomodulators against degenerative diseases such as cancer (Mendis and Simsek, 2014), and they can help reduce cardiovascular diseases (Dubois-Deruy et al., 2020). Another interesting application is in the polymer industry. González et al., (2016) used the "nejayote" as an agglutinant to form carbon black (CB) agglomerates. After analysing the properties, it was concluded that it could be used as an agglutinant not only for CB but also for other materials with applications in the wiring or insulator industry. Apart from these attempts to valorise this waste, there is no research work where this waste could be used as raw material for the manufacture of bioplastics processed by injection moulding. Therefore, basic research to test the suitability of this waste for processing by common processing methods could stimulate new applications for this current waste. For example, one alternative for this waste could be the production of bioplastics, where the choice of suitable plasticisers is key.

This work aims to revalue this waste from the maize-snack industry to produce bioplastic materials as an alternative to conventional plastics. Previous results reported in the bibliography did not use a waste stream from the food industry to generate bio-based materials. Furthermore, there has not been a systematic study where the effect of the combination of Gly:H_2O as plasticisers was evaluated in complex raw materials. To overcome these limitations, the waste stream from the maize-snack industry (nejayote) was milled and freeze-dried, obtaining a raw material (NL) used for producing bioplastics. NL was mixed with Gly and H_2O into a two-blade counterrotating rheometer at 1:0, 2:1, 1:1, 1:2, and 0:1 Gly:H_2O ratios. Blends were analysed before and after injection moulding by DMA tests. Tensile tests were also performed on the final samples. Moreover, its potential application as absorbent material was evaluated by its water uptake capacity (WUC). Finally, the structure of bioplastics after water absorption was determined by SEM tests.

2. Material and methods

2.1. Materials

The raw material used in this work was provided by Chavez & Clark, SL (El Puerto de Santa María, Cádiz). It came from the corn nixtamalisation process, which consists mainly of the external remains of the maize kernels and, to a lesser extent, whole kernels that could not be separated. Briefly, maize underwent a cooking process with water and calcium hydroxide ($Ca(OH)_2$). The grain was cooked at pH 11.0 for 30 min at a high temperature (100 °C). This basic environment weakened the pericarp to achieve its softening, in addition to gelatinization of the starch present in the endosperm (Santiago-Ramos et al., 2017). After cooking, the maize was left to rest with the cooking liquid for approximately 10 h, causing calcium and water to enter the kernel, resulting in a grain that was easy to handle. The cooked maize was then washed, thus neutralising and eliminating any possible residue and part of the pericarp that was released after cooking (Castro-Muñoz et al., 2019). This residue is usually known as nejayote and it has been used in this work to generate bioplastics. The residue arrived stored in plastic bags and refrigerated, with an appearance similar to a wet paste, being ground in a Thermomix-type mixer, Ironmix model (Cecotec, Spain), at maximum speed and room temperature for a total time of 10 min. This blender had similar performance to a standard Thermomix, with the ability to produce a slurry with temperature and speed control. Subsequently, it was frozen at −40 °C for 24 h and introduced into a LyoQuest freeze dryer (Telstar) with a condenser temperature (cold trap) of −80 °C and a pressure of 0.1 mBar, until the sample was dried. The flour obtained (NL) was kept refrigerated until use.

2.2. Methods

2.2.1. Composition of the NL residue

The proximate composition of the NL raw material was obtained prior to any experiment. Official methods of analysis (AOAC, 2023) were followed for the proximate composition. The nitrogen content was determined following the Dumas method by using a CHNS microanalyser (Leco Corporation, USA). The total protein content was obtained using the 6.25 nitrogen conversion factor (protein = % N x 6.25) (FAO, 2003). The moisture content, expressed as mass loss, was evaluated after placing 5.0 g of the sample in a Selecta oven (Barcelona, Spain) for 24 h at 105 °C. Ash content was reported as the percentage of the NL sample remaining after calcination (550 °C) in a Hobersal muffle furnace (Barcelona, Spain) for 5 h. Carbohydrate content was determined according to the ISO 6493:2000 for the determination of starch content (ISO 6493, 2000), and cellulose by the 32–05.01 AACC method for total dietary fibre (AACC, 2000).

2.2.2. Generation of bioplastics

A two-step process was used to obtain the bioplastic materials produced in this work (Álvarez-Castillo et al., 2021a). First, the biopolymer (NL) and the plasticisers (PL: Gly and H_2O) were mixed into a two-blade counter-rotating rheometer (Haake Polylab QC, ThermoHaake) at 25 °C and 50 rpm for 15 min in an appropriate ratio since it allows the measurement of torque and temperature during mixing. The ratio of biopolymer to plasticiser (i.e. NL/PL) was kept constant at 60/40, as this ratio has been reported to be suitable for other bioplastics based on rice bran, soya and egg white (Alonso-González et al., 2021a; Félix et al., 2015), while the Gly:H_2O ratios evaluated were 1:0, 2:1, 1:1, 1:2 and 0:1. After 15 min of mixing, dough-like materials were obtained and processed by injection moulding (MiniJet II, ThermoHaake) for obtaining the probes for further testing. The injection pressure used was 500 bar (20 s), while the packing pressure was 200 bar (300 s). The preheating temperature selected for the cylinder was 60 °C, while the mould temperatures were fixed at 120 °C. Other bio-based materials processed by injection moulding have used similar processing conditions (López Rocha et al., 2020; Pappu et al., 2019). Rectangular specimens (60 × 10 × 1 mm) were obtained for rheological, mechanical, and water uptake tests.

2.2.3. Rheological characterisation of blends and bioplastics

DMA tests were performed in the DMA850 (TA Instruments, Wakefield, MA, USA) to obtain the dependence of viscoelastic moduli (E′ and E″) on frequency or temperature. The mechanical spectra of the blends

and the bioplastics produced were obtained by frequency sweep tests (from 0.1 to 1 Hz at a 25 °C). In addition, the dependence of the viscoelastic moduli (E′ and E″) with temperature was obtained by temperature ramp tests (from −20 to 150 °C at 1 Hz). Prior to these measurements, strain sweep tests at 1 Hz were performed to select a deformation within the linear viscoelastic range (LVR). The parallel plate geometry (12 mm diameter) was used for blends in compression mode, while rectangular probes were used for bioplastics in tension mode (Panwar and Pal, 2017).

2.3. Rheological characterization of bioplastics

The mechanical spectra of the produced bioplastics were obtained by frequency sweep tests (from 0.1 to 1 Hz at a 25 °C), while the dependence of the viscoelastic moduli (E′ and E″) with temperature was obtained by temperature ramp tests (from −20 to 150 °C at 1 Hz). These measurements were carried out in the DMA850 rheometer for solid materials (TA Instruments, Wakefield, MA, USA). The tensile mode was selected for rectangular probes using the tensile clamp geometry. Both tests were performed within the LVR previously determined by strain sweep tests at 1 Hz (Ahmad et al., 2017).

2.3.1. Mechanical properties of bioplastics

Tensile tests were carried out to obtain stress-strain curves. These tests were performed in the Insight 10 kN Tensile Tester (MTS, MN, USA). The rectangular probes tested were deformed to failure at a constant strain rate of 1 mm min^{-1} at room temperature. Young's modulus (E), maximum stress (σ_{max}) and strain at break (ε_{max}) were determined from the stress-strain curves obtained. Tensile tests were carried out according to ISO 527-1:2019 (2019).

2.3.2. Water uptake capacity (WUC) and soluble matter loss (SML) of bioplastics

The WUC and the SML capacity of the bioplastic produced from the NL residue were analysed using a modification of the ASTM D570 standard (ASTM, 2022). Briefly, bioplastics were dried at 50 °C for 24 h in a Selecta oven (Barcelona, Spain) (w_1). They were then immersed in 100 ml of deionised water for 24 h. The probes were then removed and gently dried (w_2). Finally, the probes were lyophilised (w_3). The samples were weighted in each stage (w_1, w_2 and w_3 represent the respective weights). WUC and SML were calculated according to eqs. (1) and (2):

$$WUC\ (\%) = \frac{(w_2 - w_3)}{w_3}.100 \quad (1)$$

$$SML\ (\%) = \frac{(w_1 - w_3)}{w_1}.100 \quad (2)$$

2.3.3. Scanning electron microscopy (SEM) of freeze-dried bioplastics after water uptake

The bioplastics obtained were observed by SEM microscopy after WUC and subsequent lyophilization, while maintaining the porous structure formed. Small samples (1 × 1 cm^2) were gold coated (AuPt, 12 nm) and examined by SEM microscopy using a ZESS EVO microscope (Oberkochen, Germany). The samples were observed at a working distance of c. a. 4 cm, using an acceleration voltage of 10 kV and a beam current of 86 pA. Bioplastics from the invasive algae *Rugulopteryx okamurae* were observed in a similar way (Santana et al., 2022).

2.4. Statistical analysis

At least three independent replicates of each measurement were carried out (n = 3). Statistical analyses were performed using one-way analysis of variance (ANOVA, $p < 0.05$) using the software STATGRAPHICS 18 software (Statgraphics Technologies, Inc, NJ, USA). The uncertainty was expressed as a standard deviation (SD).

3. Results and discussion

3.1. NL residue composition

Analysis of the NL raw material showed a starch content of 74.8 ± 1.0 % and a protein content of 11.05 ± 0.8 %. Starch is found in the endosperm of the maize grain, which has a much larger surface area than the thin layer of pericarp that is to be removed after nixtamalisation. The pericarp of the maize grain is therefore eliminated during cooking (with $Ca(OH)_2$). However, some of the starch in the grains is released into the medium. As maize is a cereal, this is consistent with these results where the main component of the residue is of starch, which is the main component of cereals (Ai and Jane, 2016). Regarding the protein content in the NL material, practically all native maize protein is separated during the nixtamalisation process, considering its natural content in maize grains (Shukla and Cheryan, 2001). Dietary fibre accounts for 10.38 ± 1.6 % of the NL residue. During nixtamalisation, the outer layer of the maize kernel disintegrates, creating holes in the husk known as percolation. These new openings in the anatomy of maize allow the cooking water to communicate with the starch (Santiago-Ramos et al., 2018). The outer part that does not disintegrate during cooking is composed mainly of cellulose. The ash content is low (3.42 ± 0.47%). However, the residue after nixtamalisation contains a higher percentage of ashes compared to the ash content of maize grains (Arendt and Zannini, 2013). This is due to the addition of $Ca(OH)_2$ during this process, which may be the origin of some of the ashes found. Finally, the minimum component of the NL residue is moisture (2.95 ± 0.23%). This result is due to its drying in a freeze drier before use to prevent the growth of microorganisms.

3.2. NL-based blends

Fig. 1 shows the torque and temperature values obtained during the mixing time of the NL-based blends at five ratios of Gly:H_2O for PL (1:0, 2:1, 1:1, 1:2 and 0:1). Torque values are related to the viscosity of the blends, while the temperature of blends can be related to the energy dissipation along with crosslinking reactions (which ultimately leads to higher torque values) (Félix et al., 2016). The data obtained for the starch content confirmed the importance of H_2O in the PL ratio, as water has been reported to play a key role in the gelatinization of starch in other bioplastics (Alonso-González et al., 2022). All the blends studied showed a similar behaviour during the mixing stage carried out. The torque values obtained showed an increasing trend as the NL and PL blends were mixed (regardless of the Gly:H_2O ratio), until a plateau value was reached. This initial maximum value was reduced to a

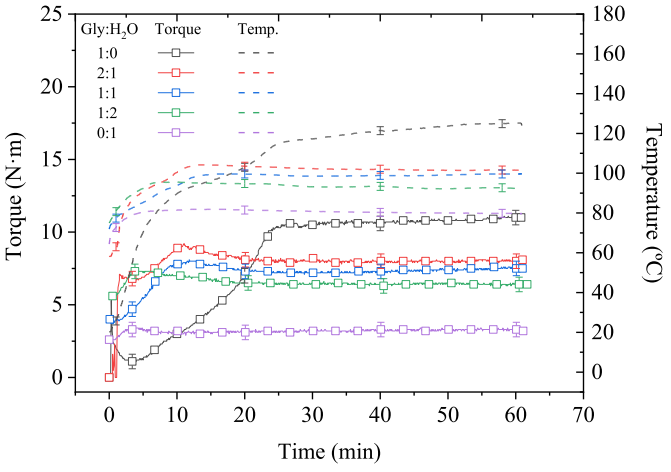

Fig. 1. Evolution of torque and temperature over mixing time of NL/PL systems at five Gly:H_2O ratios for PL (1:0, 2:1, 1:1, 1:2 and 0:1).

practically constant value and reached at shorter times as the H_2O content of the plasticiser increased. The initial increase was caused by the first movements of the rotors in the mixing chamber, where the NL and PL began to mix. During this period, a new structure began to form, which led to an increase in the viscosity of the system and consequently an increase in the energy required to homogenise the mixture (McGauran et al., 2021). In addition, the temperature values also increased, which was related to the energy dissipated by the formation of this new structure, as well as the release of energy due to the increase in friction caused by the increase in viscosity (Cheremisinoff, 2017). This behaviour is common in other bioplastics obtained from both protein systems and systems with high starch content, corroborating the obtained homogeneous mass that could be processed by injection moulding (Felix et al., 2017). However, once the maximum value was reached, the plateau torque suggested that there was no change in the structure of the blends, with the temperature data showing the same trend during this time interval (Delgado et al., 2018). With regard to the PL ratio used (Gly:H_2O), increasing the proportion of H_2O decreased the torque values of the blends, which seemed to indicate that H_2O had a greater plasticising effect than Gly in this type of system. Although the known effect of H_2O as a plasticiser is true, it must be taken into account that the materials obtained are sometimes fragile and difficult to process (Huang et al., 2019). Therefore, although the viscosity of the systems increased with the amount of Gly in the Gly:H_2O ratio, these systems must be considered for the formation of bioplastics to analyse its effect.

Dynamic mechanical analysis (DMA) was carried out to determine the viscoelastic moduli of the materials developed using small amplitude oscillatory measurements, thus determining the structure of the blends after the mixing stage. Fig. 2 shows the frequency sweeps performed on the blends to obtain the evolution of the elastic (E′) and viscous (E″) moduli within the frequency interval studied. This Figure shows a predominant elastic behaviour (even for deformable blends) since the elastic modulus is greater than the viscous one for the whole frequency range studied. It should be noted that the tan δ values (tan δ = E''/E′ and) ranged between 0.52 and 0.21, indicating that the plasticiser used had a marked effect on the flowability of the blends obtained. DMA tests also showed a directly proportional relationship between the Gly content and the value of the modules, the viscoelastic moduli decreased with the Gly content, which is consistent with the plasticiser effect of Gly in the bioplastics (Schäfer et al., 2018). These results could indicate that bioplastics with higher flexibility would be obtained with increasing GL content in the final materials. However, the mechanical properties of the processed materials may change once the raw materials are processed.

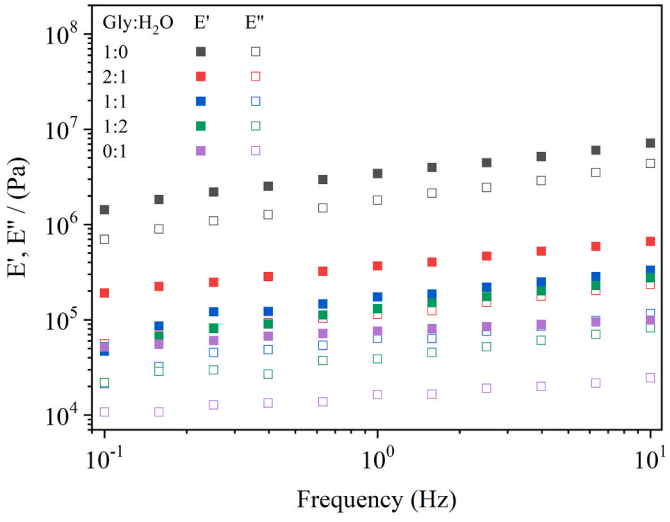

Fig. 2. Mechanical spectra obtained for NL/PL blends at five Gly:H_2O ratios for PL (1:0, 2:1, 1:1, 1:2 and 0:1).

Subsequent characterisation of the final bioplastics will elucidate the properties of the developed materials as well as the effect of the plasticiser.

3.3. NL-based bioplastics

3.3.1. Rheological analysis

After processing the blends by injection moulding, DMA analyses were carried out to evaluate the behaviour of the samples subjected to oscillatory stresses with frequency and temperature. Fig. 3A shows the frequency sweeps performed on the bioplastics obtained from the previous blends as a function of Gly:H_2O ratio (1:0, 2:1, 1:1, 1:2 and 0:1) at 60/40 NL/PL ratio, obtaining the evolution of the elastic (E′) and viscous (E″) moduli with frequency. This dynamic mechanical analysis (DMA) provides information on the behaviour of the material when subjected to a small sinusoidal stress. This figure shows that the elastic behaviour predominates in all the samples, with the elastic modulus being higher than the viscous modulus for the whole frequency range studied, which is to be expected given that the measurements were made on a solid material. It should be noted that the values obtained for these systems were higher than those previously obtained for the blends, confirming that the processing carried out on the initial NL/PL blends had structured the initial material. The values obtained (E′ at 1 Hz from 32.8 to 3.3 MPa for 0:1 and 1:0 Gly:H_2O ratios respectively) are in the range of other values previously obtained for soybean and rapeseed bioplastics (Delgado et al., 2018; Fernández-Espada et al., 2016). A direct dependence between both viscoelastic moduli (E′ and E′ E″) and frequency was observed, as they increased with increasing frequency. This type of behaviour is common in polymeric viscoelastic materials, where a certain relaxation time can be observed (Cho, 2016). In any case, the Gly:H_2O ratio influenced the rheological behaviour of the final materials obtained. Thus, the higher content of Gly was associated with a greater dependence of viscoelastic moduli with frequency as well as a decrease in their values (contrary to the results observed for the blends). This result indicated that this component was a better plasticiser of the biopolymer used, as it allowed the mobility of the polymer chains to a greather extend (Uitto and Verbeek, 2019). Thus, as the amount of Gly decreased, bioplastics with greater flexibility were obtained, which was opposite to the results obtained for blends. In this case, the flow resistance of the blends containing a greater amount of H_2O in the plasticiser blend was lower as the content of H_2O increased. This change could be related to the injection moulding process where the H_2O present in the blends could evaporate. This resulted in stiffer samples with higher values for both viscoelastic moduli. A similar behaviour was observed for rice bran samples processed with Gly:H_2O mixtures as plasticiser (Alonso-González et al., 2022).

Fig. 3B shows the evolution of the elastic (E′) and viscous (E″) moduli with temperature for the bioplastics obtained as a function of Gly:H_2O ratio (1:0, 2:1, 1:1, 1:2 and 0:1) at 60/40 NL/PL ratio. Consistent with the frequency sweep tests, the values of E′ were higher than those of E″, regardless of the temperature at which the materials were evaluated. Furthermore, the modulus values were inversely proportional to temperature (*i.e.,* they decrease as the temperature value increases). This behaviour is typical for polymeric and biopolymeric materials and is attributed to the increase in molecular mobility due to the increase in temperature, which causes a decrease in physical interactions due to thermal agitation (De Nardo and Farè, 2017; Delannoy et al., 2023). Thus, there is a structural relaxation induced by the increase in temperature, the mixtures pass from a glassy state to a rubbery state characterised by a decrease in both E′ and E'' (Hirschberg et al., 2019). This behaviour is completely similar to that of other bioplastics (and polymers), indicating that the behaviour of the material obtained from the processing of nachos waste is similar to other materials reported in the literature (Tsang et al., 2019). Regarding the evolution of the viscoelastic properties with the different proportions of Gly: H_2O plasticisers, the same proportional trend was observed, with the values of both

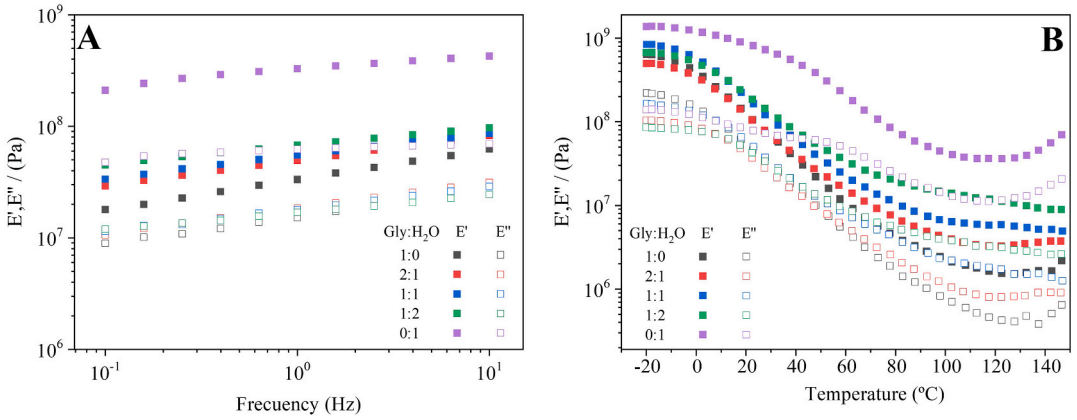

Fig. 3. Mechanical spectra (A) and evolution of viscoelastic moduli with temperature (B) obtained for NL/PL bioplastics at five Gly:H_2O ratios for PL (1:0, 2:1, 1:1, 1:2 and 0:1).

moduli decreasing as the amount of Gly in the plasticiser mixture decreased. Moreover, only systems containing a single plasticiser (either, Gly or H_2O) were those that increased their viscoelastic moduli (thermosetting potential) at higher temperatures, a behaviour typical of protein-containing bioplastics and usually attributed to crosslinking reactions (Chacón et al., 2019; Gonçalves et al., 2021).

3.3.2. *Tensile tests*

Fig. 4 shows the stress-strain curves obtained from uniaxial tensile to probe failure as a function of Gly:H_2O ratio (1:0, 2:1, 1:1, 1:2 and 0:1) at 60/40 NL/PL ratio. This Figure demonstrated the characteristic behaviour of polymeric materials, which was common to all systems analysed (Bernard et al., 2018). This behaviour is characterised by an initial increase that is directly proportional to the applied stress (elastic deformation), followed by a zone in which the stress decreases in relation to the strain (plastic deformation). Finally, there is the appearance of a neck, characterised by an abrupt decrease in the measured stress. Note that all materials showed a ductile fracture, characterised by a small fraction of material holding the material together before complete fracture (Romani et al., 2019; Wagner et al., 2018). The slope of the initial linear increase corresponds to the values of Young's modulus (E), which is related to the resistance to deformation in the early stages of the test.

The mixture composed of a 0:1 Gly:H_2O plasticiser ratio had the highest initial slope, while the 1:0 Gly:H_2O ratio had the lowest value.

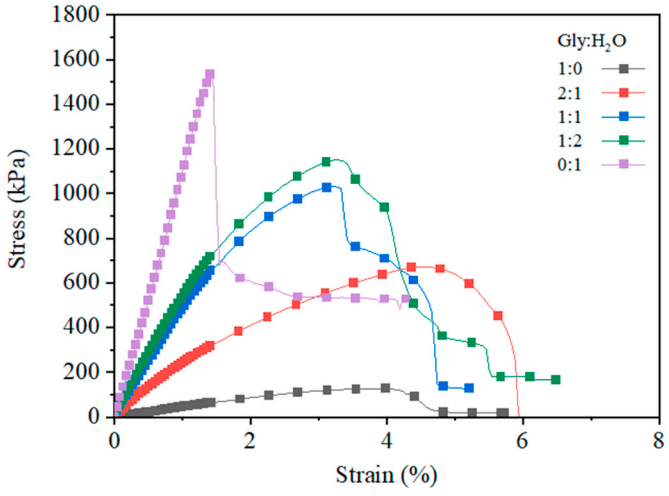

Fig. 4. Stress-strain curves obtained for NL/PL bioplastics at five Gly:H_2O ratios for PL (1:0, 2:1, 1:1, 1:2 and 0:1).

Thus, there was an inversely proportional relationship between the Young's modulus values and the different plasticiser mixtures: as the amount of Gly decreased, the E values increased up to 100 ± 10 MPa (*i.e.,* stiffer materials were obtained). Furthermore, the same proportional relationship was observed between the amount of H_2O in the mixture and the maximum stress (σ_{Max}) value obtained, which was highest for the 0:1 Gly:H_2O system (1.23 ± 0.23 MPa). As for the maximum deformation (ε_{Max}), higher values were obtained as the Gly content increased (reaching to 5.9 ± 2.9 for the 1:0 Gly:H_2O ratio). In this case, the relationship between these values and the amount of Gly was directly proportional, resulting in specimens capable of experiencing greater elongation before breaking when subjected to tensile stress. In other words, less rigid and more deformable materials were obtained as the Gly content increased. These results confirm the increase in polymer chain mobility upon addition of Gly, thus confirming the role of Gly as a plasticiser for the biopolymers analysed in this work.

Table 1 shows the numerical values obtained from the stress-strain curves (E, σ_{max} and ε_{max}) for the NL/PL bioplastic materials as a function of the Gly:H_2O ratio (1:0, 2:1, 1:1, 1:2 and 0:1). The above mentioned proportionality relationships between the values of the three parameters and the different plasticiser mixtures can be also observed in this Table. These data justify the variation in mechanical properties as a function of Gly:H_2O for the PL fraction. Thus, the presence of Gly gave flexibility to the final materials, producing more flexible specimens, and when its content was reduced, stiffer and more fragile specimens were observed.

3.4. *Water absorption capacity and loss of soluble material*

Fig. 5 shows the results of the water uptake capacity (WUC) and soluble matter loss (SML) tests obtained for NL/PL (60/40 ratio) bioplastics at five Gly:H_2O ratios for PL (1:0, 2:1, 1:1, 1:2 and 0:1). This Figure showed an increasing development of WUC as the H_2O ratio in the final properties increased. However, this perception may be misleading as the three intermediate Gly:H_2O ratios (2:1, 1:1 and 1:2) show similar WUC values. This result could be related to a porous

Table 1
Parameters obtained from stress-strain curves of NL/PL bioplastics at five Gly:H_2O ratios for PL (1:0, 2:1, 1:1, 1:2 and 0:1). Different letters within a column indicate significant differences ($p < 0.05$).

Gly: H_2O	E (MPa)	σ_{max} (MPa)	$\varepsilon_{max.}$ (%)
1:0	4.0 ± 0.6^{a}	0.11 ± 0.04^{a}	0.059 ± 0.029^{a}
2:1	28 ± 1^{b}	0.65 ± 0.03^{b}	0.050 ± 0.003^{a}
1:1	40 ± 8^{c}	1.04 ± 0.14^{c}	0.045 ± 0.010^{b}
1:2	52 ± 5^{d}	1.10 ± 0.14^{c}	0.043 ± 0.005^{b}
0:1	100 ± 10^{e}	1.23 ± 0.23^{d}	0.018 ± 0.005^{c}

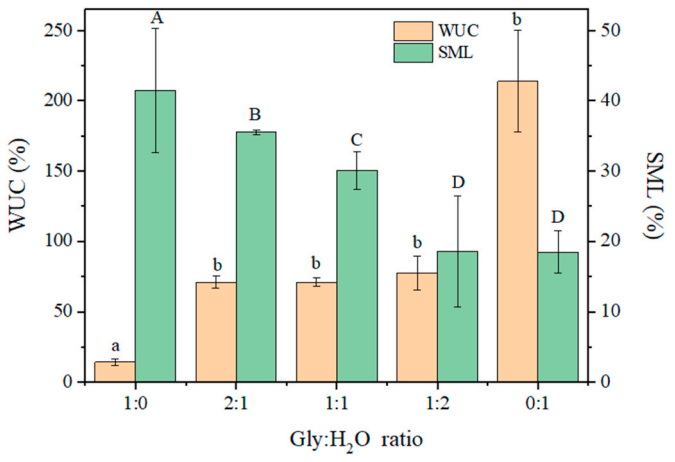

Fig. 5. Water uptake capacity (WUC) and soluble matter loss (SML) obtained for NL/PL bioplastics at five Gly:H_2O ratios for PL (1:0, 2:1, 1:1, 1:2 and 0:1). Different letters above bars indicate significant differences ($p < 0.05$).

structure developed during the packaging of the samples in the injection process, which can be caused by the evaporation of the water contained in the formulation, causing voids and cracks in rice-bran based bioplastics (Alonso-González et al., 2021b). The same trend was observed for the SML since it decreased as the amount of Gly in the plasticiser increased (ranging from 14.2 ± 2.6 to 214 ± 36% for the 1:0 and 0:1 Gly:H_2O ratios, respectively). This result can be understood because the loss of soluble material is related to the loss of plasticiser (Álvarez-Castillo et al., 2020). Thus, if some of the H_2O present in the formulation was lost during processing (as mentioned earlier in the discussion), the proportion of plasticiser that can be lost was also lower. Finally, it should be noted that, although it is true that the materials obtained do not have superabsorbent properties, the intermediate proportions give rise to materials that can be considered absorbent (Álvarez-Castillo et al., 2021b). It should be noted that, after the WUC tests, the samples with the 1:0 and 0:1 Gly:H_2O ratios showed an amorphous structure, while the 2:1, 1:1 and 1:2 Gly:H_2O ratios maintained the structure after immersion in water.

3.4.1. Scanning electron microscopy

Fig. 6 shows the SEM microscopy results obtained for the NL/PL bioplastics at five Gly: H_2O ratios for PL (1:0 (A), 2:1 (B), 1:1 (C), 1:2 (D) and 0:1 (E)). These images were taken after water uptake and further lyophilization, preserving the microstructure of the sample after swelling. The SEM images obtained reveal that the samples showed greater deformation as the amount of Gly in the plasticiser blend (PL fraction) decreased, with the presence of larger pores (average pore size increased from 22.3 to 63.4 μm). This difference in pore size is particularly evident when comparing the 1:0 and 0:1 samples. The water absorption results indicated that the use of H_2O as a plasticiser resulted in higher water absorption, as discussed above, resulting in a structure with a higher number of internal pores that allowed later water absorption. These channels are required for water penetration, which was a key stage in the water absorption capacity of polymeric materials. Thus, according to various theories of water absorption, the formation of these channels is required for the penetration of water molecules (Yan et al., 2022). Furthermore, polymer-liquid interactions also play a key role in water uptake (Hummel et al., 2020). Although Gly is a polar soluble plasticiser, the structure of those probes containing H_2O in their formulation was assembled with the solution that later to be absorbed, resulting in a microstructure that was more susceptible to subsequent water uptake.

4. Conclusions

The results obtained showed that it was possible to obtain bioplastics from the solid fraction of the maize snack industry residue known as “nejayote”, if the chosen plasticiser was suitable, suggesting a way to valorise this waste. The different Gly:H_2O ratios tested (1:0, 2:1, 1:1, 1:2, and 0:1) were feasible for its processing. However, the resulting properties depend on this ratio.

A higher water content produced blends with lower viscosity, which was reflected in the torque values during mixing and in the values of the elastic modulus values. However, when the blends were processed by injection moulding, the materials with the highest elastic moduli were those with a higher H_2O content, due to the loss of plasticiser by evaporation. Thus, H_2O as a plasticiser made the blends easier to process (E'_1 decreased from 3.43 ± 0.21 MPa to 76.25 ± 0.53 kPa for the 1:0 and the 0:1 Gly:H_2O ratios, respectively), while Gly resulted in more flexible

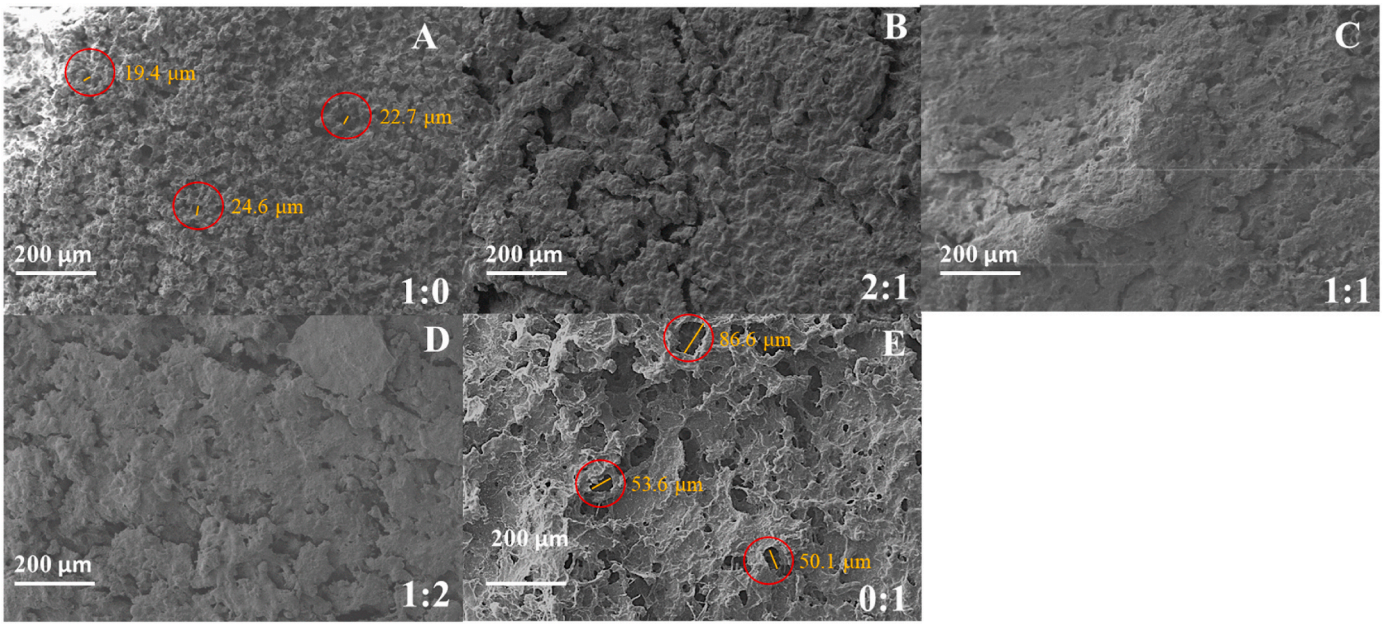

Fig. 6. SEM images obtained for NL/PL bioplastics at five Gly:H_2O ratios for PL: 1:0 (A), 2:1 (B), 1:1 (C), 1:2 (D) and 0:1 (E).

bioplastics. Thus, the loss of plasticiser during the processing of the blend (*i.e.,* H_2O) resulted in more rigid samples (lower polymer chain mobility) with defects due to its evaporation during processing, which can limit the use of this plasticiser. This behaviour was observed in the frequency sweeps (E′ increased from 33.4 to 328 MPa for 1:0 and 0:1 Gly:H_2O ratios, respectively) and in the temperature ramps performed, where the viscoelastic moduli decreased less for the 0:1 Gly:H_2O ratio. This bioplastic contained the highest amount of water in the NL fraction, and it also exhibited the highest WUC and the SML. However, intermediate Gly:H_2O ratios had similar water absorption values. The micrographs obtained showed a generally homogeneous structure with the appearance of pores that allow water absorption; these pores were significantly smaller at a higher concentration of Gly.

The results obtained indicate that it is possible to obtain bioplastics from a waste product of the maize snack industry, allowing the replacement of some of the current plastic materials with others based on biopolymers, leading to a circular economy. For future work, we need to test these materials under real working conditions in the desired end application, which could include active packaging applications such as absorbing liquids in the food industry and to extend the shelf life of food products.

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Author's Contribution

Rosario Salas Cardenas: Data curation, Formal analysis, Investigation, Visualization. Manuel Felix Angel: Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – original draft. Manuela Ruiz: Conceptualization, Formal analysis, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – review & editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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