STUDY OF THE CONCENTRATION EFFECT OF GLYCEROL AND TRIETHYL-CITRATE PLASTICIZERS IN THE THERMAL AND BARRIER PROPERTIES OF PLASTICIZED CELLULOSE ACETATE FILMS

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RESUMO

Abstract: Biologically based polymeric packaging has been used as an alternative to petroleum-based polymers, as these are harmful to the environment. In this context, the development of cellulose acetate (CA) films deserves to be highlighted because it is a low-cost polymer, non-toxic, and biocompatible with a series of solvents for film formation, is also derived from cellulose, which is the most abundant renewable polymer on Earth. Although promising, the use of CA as packaging material requires the addition of processing aids, such as plasticisers, in order to improve the flexibility, workability, or distensibility of the polymer. In this regard, this work aimed to optimize the effect of concentrations (1.8, 3.6, 5.4, and 7.2 mols) of two plasticizer types, glycerol (GLI) and triethyl citrate (TEC), added into the polymeric matrix of CA, produced by the casting method, using acetone as a solvent. In addition, the study aimed to characterize the film properties through molecular, thermal , barrier and water vapor analyses. The addition of higher molar concentrations of both plasticizers induced physical and chemical variations. By thermogravimetric analysis, it was possible to observe that the films with higher molar concentrations, presented less thermal stability. The films plastified with GLI, showed increased permeability to water vapor. In summary, it is recommended that both plasticizers can be used in polymeric dispersions of CA, for the development of food packaging.

1. Introduction

Plastic packaging has been widely used around the world due to its ease of production and convenience during its application as packaging for products, especially for food. However, the pollution caused by plastic packaging is a critical environmental problem, considered cross-border and universal, which requires various solutions, such as the use of technology that promotes sustainability, systematic efforts in environmental management, behavior change and, the use of waste recycling. In the absence of recycling programs, the accumulation of plastics in nature causes serious damage to the ecosystem, and to animal and human health, which increasingly suffer from climate change. Therefore, with urgency to address this issue, the government, the private sector, civil society and academia seek immediate responses to act effectively for the balance of the environment (BRAUN; TRAORE, 2015; BOUCHER; et al., 2020). Thus, the development of packaging with bio-based polymers has great potential to increase sustainability and reduce adverse environmental effects, because they have high biodegradability. However, for the current scenario to change, these new packages must have mechanical, thermal and barrier properties similar or better than petrochemical products, in addition, they should have an accessible price. In this context, there is a great interest in the use of cellulose acetate (AC) as a polymeric matrix for food packaging production, due to its biodegradability properties, for being non-toxic, odorless and compatible with several solvents, such as acetone, and also for being derived from cellulose, the most abundant renewable polymer on Earth (MILOVANOVIC et al., 2016). Although cellulose acetate has numerous advantages, there is a need to add plasticizers to improve the barrier against external agents, improve mechanical properties, and increase the flexibility of the final product. To date, glycerol, sorbitol, xylitol (MURRIETA-MARTÍNEZ et al., 2019) and polyethylene glycol (DARIE-NIŢĂ et al., 2016),dair have been widely applied as plasticisers in

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plastic films. Therefore, in this study, we aimed to optimize the effect of concentrations (1.8; 3.6; 5.4 and 7.2 mols) and types of plasticizers, glycerol (GLI) or triethyl citrate (TEC), in the polymeric matrix of AC. Besides, techniques thermogravimetric analysis (TGA) and water vapor permeability (WVP), were used to characterize the film.

2 Material and methods

2.1. Materials

Cellulose acetate (GS = 2.5; MM = 2,024,000 g.mol-1) was donated by Rhodia Solvay Group (Santo André, SP, Brazil). Acetone, Glycerol, Triethyl Citrate and n-heptan were obtained from Sigma-Aldrich (San Luis, Missouri, USA).

2.2 Film preparation

Molar concentrations equal to 1.8; 3.6; 5.4; 7.2 of GLI and TEC plasticizers were added, individually, into 10 % AC dispersion in acetone, sealed and kept to rest for 24 hours. Subsequently, the polymeric dispersion was homogenized manually for 2 min, out into glass plates (25 x 10 cm^2), where remained for the solvent evaporation (25 ºC + 2 ºC). The films were stored under a vacuum in polyethylene/nylon packages until the moment of their use.

2.3 Thermogravimetric analysis (TGA)

The TGA of the films was made in DTG thermal analyzer (SHIMADZU, model 60H, Japan). Approximately 4 mg of each film packaged in alumina pans were heated in a temperature range from 30 °C to 600 °C at a heating rate of 10 ºC.min-1, in a nitrogen atmosphere, with a flow of 50 mL.min-1. The thermal stability of the samples was evaluated by thermogravimetric curves (TG) and the TG derivative (DTG).

2.4 Water vapor permeability (WVP)

The WVP of the films was determined gravimetrically, according to ASTM E96/E96M (ASTM, 2005), with modifications (Olivato et al., 2012). Before the analysis, the samples were conditioned at 25 ºC + 2 ºC and 53% relative humidity (UR) for 12 h. The films were cut in circular shape (Ø = 80 mm) and sealed with liquid paraffin at the film/paraffin-capsule junction. The inside of the capsules was filled with LiCl saturated solution (12% UR). This system was stored at 25 °C + 2 ºC, inside of a desiccator containing saturated NaCl solution (75% UR), which promoted a constant UR gradient (63%) through the film. The samples were weighed every 3 h during 72 h of testing. The mass gain (m) was plotted as a function of time (t) and the slope of the curve was calculated by linear regression (R2>0.999). The water vapor permeability rate (TWVP) was calculated by Equation 1.

Equation 1

Since m/t corresponds to the angular coefficient of the curve and A (m^2) corresponds to the permeation area of the film sample. The values of the water vapor permeability (PVA) of the films were calculated according to Equation 2.

Equation 2

Since st is the average of the sample thickness (m), sp is the saturation pressure of the water vapor at 25 °C (Pa), RH1 is the UR of the desiccator, and RH2 is the UR of the inside of the capsule.

2.5 Statistical Analysis

The data were analyzed through Analysis of Variance (ANOVA). For each response, a regression curve was adjusted, and the statistical parameters, such as the determination coefficient (R^2) and lack of adjustment (Faj) (with 5% probability significance) were obtained when it was possible, taking into consideration the evaluated factors. All statistical analyses were performed with Minitab statistical program, version 17 and Origin Pro 8.5.

3 Results and discussion

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3.1 Thermogravimetric Analysis (TGA)

The thermogravimetric curves (TGA) of the plasticized films and their derivatives (DTG) are shown in Fig.1. Mass losses (%) of the samples were plotted as a function of temperature (°C), ranging from 25 °C to 600 °C. Through the TGA technique, it was possible to observe two main events of the thermal decomposition of the control film, in which the initial phase occurred between the temperatures of 25 °C and 120 °C, related to the evaporation of free water. The second event occurred between temperatures of 312.8 °C and 394.1 °C, a mass loss of 74% (m/m) occurred due to the decomposition of the AC polymer (BASHA and MORSI 2017). TG and DTG curves for films plasticized with GLI are represented in Fig.7 (a) and (a'). Three events were observed for this treatment, the first event occurred in the temperature range of 33.1 °C and 100.9 °C, related to the free water losses. The second event occurred at 145.7 °C initial temperature, and corresponds to the evaporation of water delimited in the system, also to be allocated to gli degree, where the piece grows with the growth of gli. The third event occurred in the temperature range of 335 °C to 409.6 °C, in which a mass variation from 55.2% to 61.5% (m/m) was observed, and this behavior can be attributed to the decompositionAC polymer chain. The thermal degradation of films plasticized with GLI occurred at lower temperatures than non-plasticized films and this effect is due to the distancing of the AC chains caused by the insertion of GLI interlaced (DÍAZ-GALINDO et al., 2020; LIANG; WANG, 2018). Similar events were observed in the TG and DTG curves according to Fig. 7 (b) and (b'), for films containing TEC plasticizer. The first event occurred in the temperature range of 30.5 °C to 116.3 °C, and 0.2% to 2.7% (wt.) mass losses was noted, corresponding to the loss of free water. This behavior happed due to the enhancement of the distance between the polymeric chains causing, consequently, higher mobility of the water. As the TEC concentrations increased into the AC matrix, the temperature of this event reduced. The second event occurred at temperatures of 138.8 °C to 328.6 °C, attributed to the decomposition of the TEC and the evaporation of water delimited in the system, where, major molar concentrations of tec, indicate risk right.The third event occurred in temperature ranges of 217.5 °C to 407 °C, corresponding to AC degradation. Similar effects of thermal degradation were observed in poly (lactic acid) based films (PLA) developed by Maiza et al. (2015).

Fig 1. Thermogravimetric curves (TGA) (ou TG?) (a) and (b) and their derivatives (DTG) (a') and (b') for plasticized films with different concentrations of GLI and TEC respectively.

3.2 Water vapor permeability

WPV determination is one of the most important properties for polymers, especially for biopolymers. It is crucial to correlate specific requirements, according to the intended end use, to predict the useful life of food (KANATT et al., 2012). Packaging materials should have lower WPV values to avoid moisture exchange between environment and food (PARK et al., 2003).

The results of WVP analysis are displayed in Fig.2. WVP of the films increased as the plasticizer molar concentrations were boosted. Films plasticized with TEC exhibited WVP values lower than that plasticized with GLI, and this effect can be associated with the heterogeneity of GLI films, that provide enough distance between their polymeric chains and pores formation, facilitating the water vapor pathway (RHIM; LEE; HONG, 2011). Similar results were reported for films produced with Artemisia sphaerocephala Krasch gum by Liang and Wang (2018). Corroborating with the results, Sothornvit and Krochta (2001) observed the increase of WPV films with the increment in the plasticizer molarities caused due to the reduction of intermolecular forces between polymer chains. They also point out that, GLI is a hydrophilic plasticizer capable to absorb significant amounts of water to the biopolymer structure, due to its remarkable hygroscopic property, increasing WPA

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values (SOTHORNVIT; KROCHTA, 2001).

WVP control film was higher than the WVP of the plasticized films, regardless of the molecular structure of the plasticizing and their concentration, which confirms the interaction between the plasticizers and the polymeric chain of AC films even in low concentrations.

Fig.2. Water vapour permeability of AC films plasticized with GLI and TEC.

Averages followed by the same letter do not differ according to Tukey's test ($p \leq 0, 05$).

Conclusion

In this study GLI and TEC plasticizers were used, in different molar concentrations, to analyze the physicochemical properties for the development of CA packaging, which although already widely used, studies are lacking to understand the influence of these plasticizers in this matrix, which are biodegradable packaging, useful to substitute several pollutant polymers of petrochemical origin. In this circumstance, the addition of different molar concentrations of GLI and TEC, presented interesting and highly different characteristics, according to the properties analyzed. The use of both plasticizers, showed good results as to thermal stability.Films developed with TEC, showed better water vapor protection. In summary, both plasticizers can be used for the development of packaging for the food industry, in which it is suggested that each property be analyzed separately, so that the ideal packaging can be chosen according to the purpose of use.

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