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POLYSTYRENE/THERMOPLASTIC STARCH BLENDS WITH DIFFERENT PLASTICIZERS

Preparation and thermal characterization

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Conventional plastics has a large impact in increasing the environment's pollution. That's why the interest has turned towards novel partially and completely biodegradable polymers. In this work, blends of polystyrene and thermoplastic starch with glycerol and Buriti (*Mauritia flexuosa* L.) oil as plasticizers were prepared. Samples were analyzed using TG/DTG and DSC techniques. The TG results indicated that the blends with Buriti oil are thermally more stable than those with glycerol. The DSC analysis that Buriti oil provides a higher degree of plasticization of PS, compared to the blends plasticized using glycerol under the studied conditions.

Keywords: *Buriti oil, glycerol, thermal analysis, thermoplastic starch*

Introduction

Conventional plastics prepared from fossil fuels are not only non-renewable and finite resources, but cause also troubles in waste treatment since they are inert against the attack of microorganisms [1]. The continuous increase of environmental pollution has lead to the development of biodegradable polymers, applied mainly in the food packaging and agriculture decreasing the environmental pollution [2].

Polystyrene (PS) is a versatile thermoplastic polymer used in a wide range of durable and single use applications. PS is among the most dominant packaging materials nowadays, however it does not decompose itself. Similarly to other packaging materials, when the PS products reached their application, most of them are deposed in open dumps, landfills, or as simple litter [3].

Addition of different starches e.g. cassava (Manihot esculenta Crantz) to PS aims to achieve biodegradability [3]. These starch polymer blends are biodegradable since the removal of starch by microorganisms can cause severe reduction in the mechanical strength of the remaining non-biodegradable portions which disintegrate to smaller pieces [4].

Starch is a natural carbohydrate storage material, which accumulates in green plants in the form of granules. This is an alternative constituent of biodegradable plastic production because it is completely biodegradable resulting carbon dioxide and water. Since this is an inexpensive additive, it focused the attention of the polymer producing companies to its application in polymer mixtures in order of decrease the cost of the final product [5, 6].

To convert starch to thermoplastic starch (TPS) and allow its proper blending with PS it is necessary to use a plasticizer agent like water, glycerin, sorbitol, etc., at high temperature (90–180°C) and shear [6]. Mainly water and glycerol as plasticizer are used together with starch. TPS has two main disadvantages compared to most plastics currently in use, i.e. it is highly water-soluble and has poor mechanical properties. These features can be improved by mixing it with certain synthetic polymers [3, 5, 7].

In this work we investigated the properties of Buriti oil as a novel and natural plasticizer for starch. Buriti (*Mauritia flexuosa* L.) is an abundant palm in the Amazonian Region of Brazil and supplies raw material for several applications [8–11]. Supercritical CO_2 extraction of the pulp of the Buriti fruit results Buriti oil fractions with a high concentration of oleic acid, tocopherols and carotenoids, especially β-carotene [8, 9]. The aim of this work is the investigation of the thermal properties of PS/TPS blends with two different plasticizers: glycerol and Buriti oil, using TG/DTG and DSC.

Experimental

Materials

PS ($\overline{M_w}$=280000; ρ=1.047 g mL^{-1}) was purchased from Aldrich Chemical Co. and glycerol from VETEC. Dried cassava (*Manihot esculenta Crantz*)

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starch with 74.70±1.76% of amylopectin, determined by colorimetric analyses [12] was used; Buriti oil (ρ=0.86 g mL^{-1}) extracted with supercritical CO$_2$ from the shell and the pulp of ripe fruits [8] was courteously supplied by Dr. Moreira from Universidade Federal do Pará (UFPA), Brazil. Ethyl acetate (analytical grade) was also used.

Preparation of thermoplastic starch

TPS was obtained by mixing starch powder, water and glycerol or Buriti oil in 50:15:35 (mass/vol/vol) ratio according to Ramsay *et al*. [13] but after some modifications. The constituents were mixed for 30 min to obtain a paste which was transformed to TPS by heating at 95°C in water bath with continuous stirring for 30 min.

Preparation of the blends

PS and TPS were mixed in different ratios (0.9:0.1, 0.7:0.3, 0.5:0.5 and 0.3:0.7, mass/mass%) and then stirred (3 h, 50°C) with hot ethyl acetate. The blends were prepared by conventional-casting technique using Teflon^{TM} dishes as casting surfaces for at least 24 h at room temperature and vacuum (between $6.6\cdot 10^2$–$13.2\cdot 10^2$ Pa). The obtained material, with 200 to 300 μm thickness was stored far from light to avoid the decomposition of the oil.

Methods

Thermogravimetric analysis (TG) was carried out in a Shimadzu TGA-50 from room temperature to 600°C, at a heating rate of 10°C min^{-1}, under helium atmosphere (50 mL min^{-1}) in order to determine the mass loss and decomposition temperature (T_d) of the blends.

Differential scanning calorimetry (DSC) measurements were performed in a Shimadzu DSC-50 under helium flow (50 mL min^{-1}). About 5.0 mg samples were placed in aluminium pans sealed and cooled with liquid nitrogen down to –140°C for the materials with glycerol and to –100°C for materials with Buriti oil. Then, the samples were heated at 10°C min^{-1} of heating rate up to 300°C. Two heating scans were done for each sample and for the analyses the curves of the second scan were used. The mid-point temperatures of the heat capacity changes in the DSC curves were considered as the glass transition temperatures (T_g).

Results and discussion

Visually, the air-contact surface was rougher than the Teflon^{TM} contact surface of the solution cast films. The blends with Buriti oil were yellow due to the presence of β-carotene. The higher content of TPS in the blends provides more brittleness as found by Lorcks [14].

Depending on the TPS content TG and DTG curves of PS/TPS blends with glycerol (Fig. 1) present 2–4 decomposition stages. PS shows T_d at 429°C which is related to its depolymerization [15]; below this temperature the decomposition is due to the TPS. Products of pyrolytic decomposition of starch and its fractions include carbon monoxide, water, volatile organic compounds and a carbonaceous residue [16]. Addition of TPS to PS leads to a displacement of the degradation profile of blends towards temperature close to T_d of the glycerol (213°C) and starch (309°C). An increase was observed in the number of the degradation stages in the blends together with the increase of the TPS content. Figure 2 shows the TG and DTG curves of blends with Buriti oil plasticizer. For the plasticized starch with Buriti oil (Fig. 2) it is worth to say that TPS addition causes rapid thermal degradation of PS, mainly for higher ratios of TPS. Blends obtained with glycerol degrade in more stages and at inferior temperatures compared to those produced with Buriti oil. The blends having higher than 50% TPS content have more decomposition stages showing a decrease in the value of last T_d indicating the 'easier' thermal degradation. The observed mass loss is in a direct relation with the amount of starch in the blends.

According to the DSC plots of PS/TPS blends with glycerol (Fig. 3a) shows almost constant T_g values of the blends being similar to the T_g of PS, indicat-

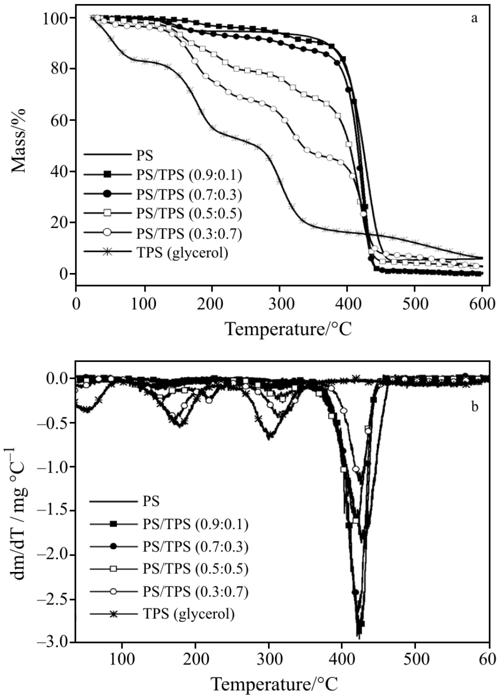

Fig. 1 a – TG and b – DTG plots of PS, TPS and PS/TPS blends with glycerol

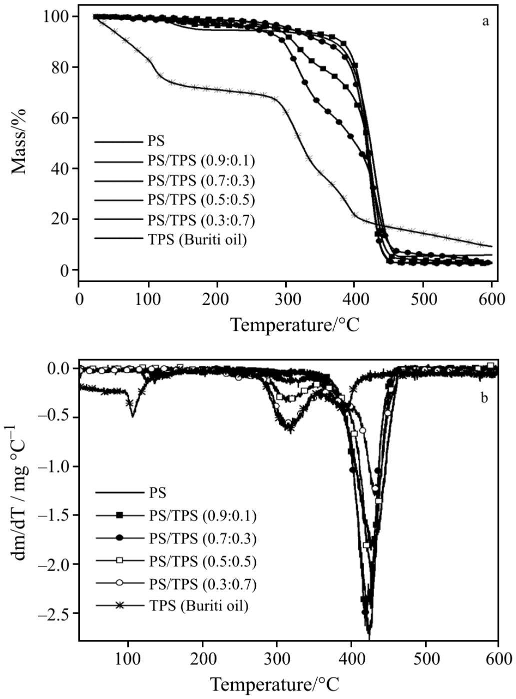

Fig. 2 a – TG and b – DTG plots of PS, TPS and PS/TPS blends with Buriti oil

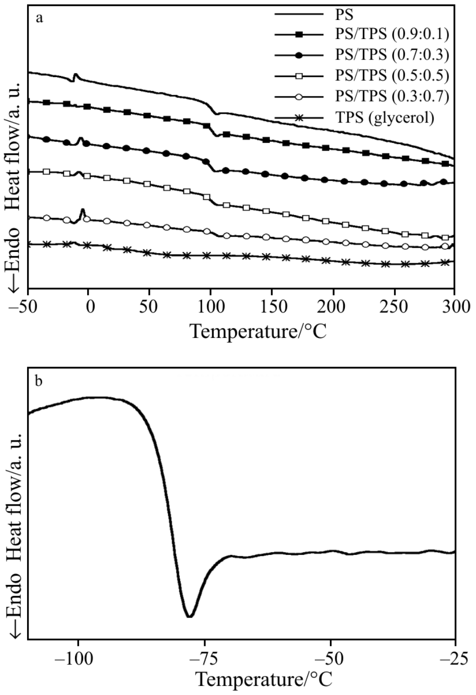

Fig. 3 DSC curves of a – PS/TPS blends with glycerol and b – glycerol

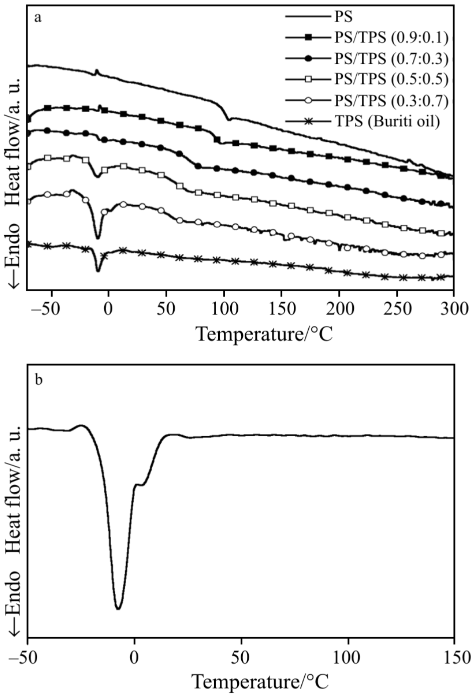

Fig. 4 DSC curves of a – PS/TPS blends with Buriti oil and b – Buriti oil

ing that the glycerol does not act as plasticizer under the studied conditions. However, this transition remains broad with the increase of TPS in the blends. According to Lourdin *et al.* [17] sometimes antiplasticization of starch takes place promoted by water or glycerol. An exothermic transition was also observed below 0°C which is related to the phase transition of glycerol in the polymeric matrix and an endothermic transition in the TPS around –10°C which is probably associated to the displacement of a glycerol phase transition close to –70°C (Fig. 3b). No endothermic transition beyond the T_g was observed from the second scan, indicating that no re-crystallization of starch molecules (retrogradation) occurred during cooling and the DSC measurements [18].

DSC data revealed that the PS/TPS blends with Buriti oil (Fig. 4a) show intermediate characteristics between pure PS and TPS. When starch was plasticized with Buriti oil (content up to 50%) the DSC profiles of the blends are very close to that of the pure PS. As the oil content increases, a small endothermic peak close to –9°C related to an oleic acid phase transition [19], was observed (Fig. 4b). In the same way, the increase of TPS content in the blends leads to a linear increase in the peak areas related to the transition of the oleic acid [20, 21]. On the contrary, for the blends with glycerol it is observed that T_g decreases as the TPS content increases in the blends, indicating that Buriti oil is a more efficient plasticizer for the studied materials than glycerol.

The irreversible order–disorder transition related to starch gelatinization it was not observed for both of the used plasticizers.

Conclusions

Thermal properties of PS/TPS blends with two different plasticizers, glycerol and Buriti oil were investigated. The thermal characteristics of the blends clearly indicate a phase separation of the non-miscible polymers.

The number of degradation steps in the TG curves of the blends increased with TPS content. Generally, blending of PS with TPS resulted less thermal stability, although the blends with TPS plasticized by Buriti oil appear thermally more stable than those with glycerol. Furthermore, the thermal stability and the mass loss of PS/TPS blends have direct relation to the ratio of TPS in the blends.

DSC data showed that addition of TPS plasticized with Buriti oil to the PS decreases its T_g, providing a larger plasticization compared to the blends plasticized by glycerol. Thus, the obtained results show that Buriti oil, a natural raw material can be used as an environmentally-friendly alternative to other materials, presents a good plasticizer effect for cassava starch and its blends with polystyrene.

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