Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 2, 529–534

THERMAL AND STRUCTURAL BEHAVIOR OF BURITI OIL/ POLY(METHYL METHACRYLATE) AND BURITI OIL/POLYSTYRENE MATERIALS

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This work reports the thermal and structural changes promoted by Buriti (*Mauritia flexuosa* L.) oil incorporation into polystyrene (PS) and poly(methyl methacrylate) (PMMA) matrices. Buriti oil, which was used due to its high β-carotene content has a good thermal stability and can provide some stability to PS and PMMA as it was shown by TG and TMA data. DSC results showed that both PMMA and PS-based materials were plasticized by the oil and demonstrated that they are immiscible materials. SEM images depict the materials' morphology.

Keywords: *Buriti oil, polymer additives, poly(methyl methacrylate), polystyrene*

Introduction

Although poly(methyl methacrylate) (PMMA) and polystyrene (PS) are widely employed in the industry, they may acquire several other uses when modified by other substances [1]. A large class of these substances are the plasticizers employed to soften materials like polymers and thus improve its processing. Despite the fact that the plasticizer market is established new investigations on the topic are still suitable given that some health and environmental aspects require discussion [1]. Efforts include searching for new plasticizers that exhibit action as thermal stabilizers without losing its low cost [1–3].

A natural, abundant, cheap and red-orange colored oil is reported here as a novel plasticizer. The Buriti (*Mauritia flexuosa* L.), an abundant palm in the Amazonian Region of Brazil supplies raw material for a variety of applications such as roots for medical use, trunks to produce wine, liqueur and canoe manufacture proving itself as an important resource for workers. The oil extracted from ripe fruits of Buriti contains high concentrations of oleic acid, tocopherols and carotenoids (Table 1), especially β-carotene which is responsible for the oil's red-orange color [4–6].

Initially it was proposed that this oil can be used as UV absorber additive in polymers [7]. Polymer matrices modified by Buriti oil (BO) can also emit light [7] and this fact encouraged its use as organic electronic device component [8].

Here, BO's performance as plasticizer for PS and PMMA was investigated, as well as the morphology and thermal stability of the materials. The advantages of these polymeric materials are their interesting properties, low cost and ready availability from a renewable natural resource.

Table 1 Typical chemical composition of the oil from the shell and pulp of Buriti extracted with CO_2 at 20 MPa and 313 K [6]

Substance	Amount
Carotenoids/ppm	1707
Tocopherols/ppm	800
Free fatty acid composition/%	
Main saturated fatty acid/%	
Palmitic	17.34–19.20
Stearic	2.00
Main unsaturated fatty acid/%	
Oleic	73.30–78.73
Linoleic	2.40–3.93
Linolenic	2.20
Some carotenoids (ppm)	
trans-β-carotene	672±10
13-*cis*-β-carotene	359±27
9-*cis*-β-carotene	150±18
α-carotene	61±7

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1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

Materials

Buriti oil (ρ=0.86 g mL^{-1}) extracted with supercritical CO$_2$ from the shell and the pulp of ripe Buriti fruits were used. Low molecular mass PMMA ($\overline{M}_w$=120000; ρ=1.188 g mL^{-1}; T_g=114°C) and PS ($\overline{M}_w$=280000; ρ=1.047 g mL^{-1}; T_g=100°C) were purchased from Aldrich Chemical Co. Analytical reagent grade chloroform was also used in all preparations.

Preparation of the mixtures

Buriti oil/PMMA and Buriti oil/PS samples were prepared by adding different amounts of BO (8, 15, 35 and 47 mass%) to the polymers in chloroform at room temperature and under continuous stirring for 4 h. Resultant mixtures were submitted to solvent casting technique using Teflon$^{\text{TM}}$ dishes for at least 24 h at room temperature and vacuum (5–10 Torr) for 4 h. Casting surfaces with thickness ranging from 200–300 μm were obtained. These were then placed in a dark environment.

Methods

Thermal analysis

Differential scanning calorimetry (DSC) data of samples (5–10 mg) were recorded in the temperature range of –100 to 250°C under a helium flow of 50 mL min^{-1} on a DSC-50/Shimadzu instrument. Samples were sealed in aluminum pans and heated at a rate of 10°C min^{-1}. Two scans were obtained for each sample and for the analyses the second scan's resulting curve was used. The temperature at the midpoint of the change in slope of the DSC heat-capacity change was taken as the glass transition temperatures (T_g).

Thermogravimetric analyses (TG) were carried out in a TGA-50/Shimadzu thermogravimetric analyzer in helium atmosphere (50 mL min^{-1}). Each sample (5–10 mg) was placed in platinum pan and thermogravimetric curves were recorded in the course of heating from room temperature to 550°C at a heating rate of 20°C min^{-1}. The decomposition temperature (T_d) of the blends was determined by derivative thermogravimetry (DTG).

Thermal mechanical analyses (TMA) were performed in a TMA-50/Shimadzu at a rate of 10°C min^{-1} from ambient temperature to 120°C at air. Samples with 0.2 to 0.3 mm of thickness were analyzed in the penetration mode with two different loads: 10 and 100 mN. The softening temperature (T_s) was obtained from the tangent of the first decay of the curve.

Scanning electron microscopy (SEM)

Surface structures of the samples were studied through scanning electron microscopy, SEM (Zeiss, mod DSM 962). The samples were fractured in liquid nitrogen, fixed on aluminum supports using silver adhesive and covered with gold (Sputter Coater Blazers SCD050). The SEM images were obtained using 15 kV and 60 μA.

Results and discussion

DSC curve of Buriti oil (Fig. 1) shows three thermal events. The first one is an exothermic peak at 24°C related to the oil's crystallization that occurs as a consequence of the abrupt cooling of the sample in course of data acquisition. The first endothermic event peak appears around –7°C (ΔH=298.1 J g^{-1}) is associated to a solid phase transition which was discussed by Cedenõ *et al.* [9] and Garcia-Quiroz *et al.* [10] and presented by Schlemmer *et al.* [11]. Another endothermic peak was observed next to 3°C and refers to the melting process, in accordance with literature [9–11].

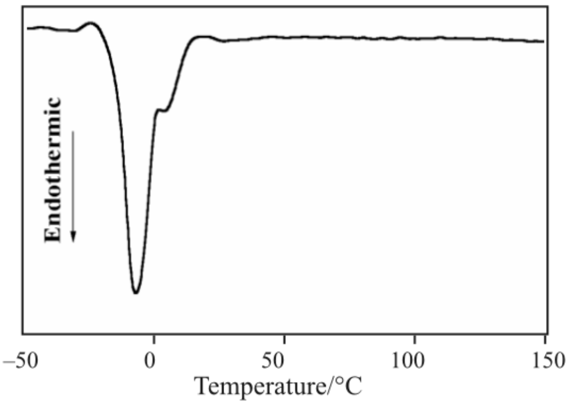

Fig. 1 DSC curve of Buriti oil

A single glass transition was recorded in the polymers thermal traces (Fig. 2). The corresponding numerical values are listed in Table 2. The plasticizing effect of BO is demonstrated through the decrease in the glass transition temperature (T_g) of the polymers. This effect is sharper in the case of PS where the T_g diminishes considerably depending on the oil content (Table 2). T_g values of PMMA are slightly changed by the addition of oil since it reduces around 20% at most. DSC curves of some of these modified materials show other thermal events associated to BO.

The occurrence of such events shows that these materials are heterogeneous mixtures, even though macroscopically they are homogeneous and no exudation was observed. Both PS and PMMA are immiscible with the oil. Therefore, the BO-polymer mixture is obtained due to their interaction with the solvent,

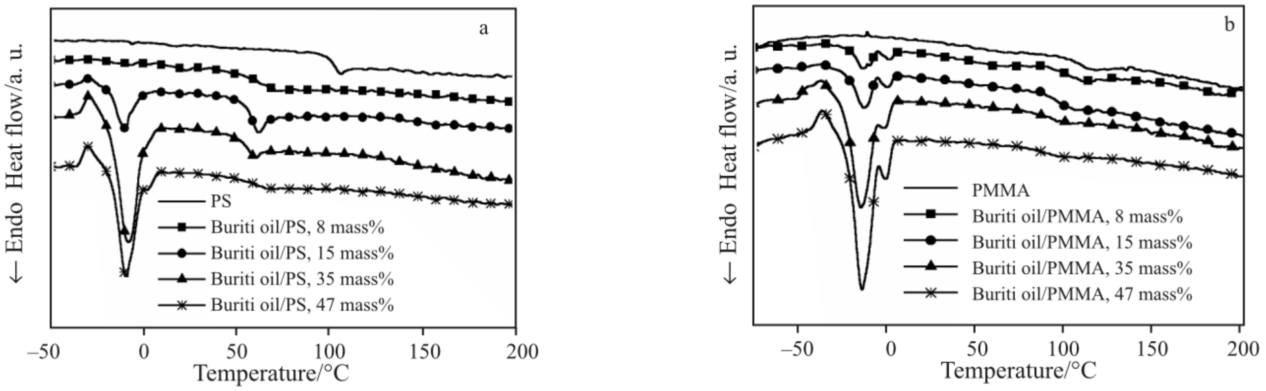

Fig. 2 DSC curves of a – PS and Buriti oil/PS mixtures and b – PMMA and Buriti oil/PMMA mixtures

constituting a ternary system. During the preparation of the polymeric solutions with BO the solvent is being evaporated, consequently the oil is then being coagulated into the polymer matrices. Phase separation is established after total solvent evaporation and thus results in materials showing distinct micro domains of BO inside the matrices (Fig. 3). The absence of phase transition (melting) peak related to BO in DSC traces of BO/PS 8.00 mass% (3°C) indicates that the oil is more compatible with PS than with PMMA.

The decomposition of Buriti oil takes place in two steps. The first one occurs near 260°C due to the release of volatile components and the second stage appears around 425°C (Fig. 4). In this stage the fatty acids break down completely. The thermal stability of BO is higher compared to other vegetable oils, such as coconut or sesame oil [12]. The influence of Buriti oil on the thermal stability of PS and PMMA was evaluated through the comparison of the thermal degradation temperatures of the blends and polymer alone.

The bulk PS and its mixtures with BO decomposed in a single step process (Fig. 5a). This process corresponds to the formation of monomers, dimers and oligomers due to random bond scission that occurs in the main chain [13]. The role of BO as PS thermal stabilizer is small when temperatures of decomposition are considered, however it is interesting to notice that the mass loss was reduced (Table 3). This happens because the constituents of oil provide a source of trapping site radicals that protect the main chain [12]. Among these constituents β-carotene and oleic acid are noticeable.

For the thermal decomposition of PMMA and Buriti oil/PMMA hybrid a three-step process (Fig. 5b) was identified. The first step takes place around 140–180°C and is related to the bond linkages of tail-to-tail bond in PMMA [13]. It appears that incorporation of Buriti oil to the polymer matrix oc-

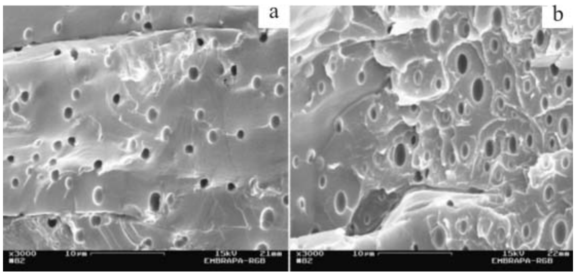

Fig. 3 SEM micrographs of a – Buriti oil/PS (8.00 mass%) and b – Buriti oil/PMMA (8.00 mass%) mixtures

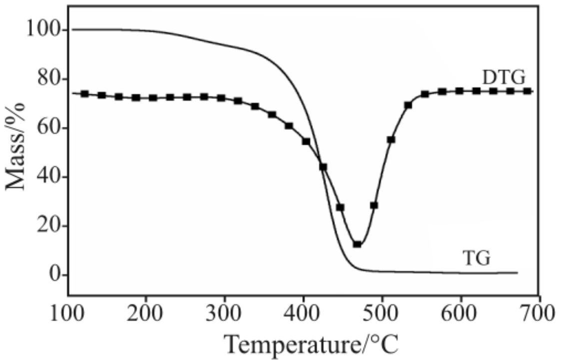

Fig. 4 TG-DTG plot of Buriti oil

Table 2 Glass transition temperature (T_g) values

Sample	T_g/°C	Sample	T_g/°C
PS	101	PMMA	110
BO/PS, 8.00 mass%	68	BO/PMMA, 8.00 mass%	102
BO/PS, 15.00 mass%	59	BO/PMMA, 15.00 mass%	97
BO/PS, 35.00 mass%	55	BO/PMMA, 35.00 mass%	94
BO/PS, 47.00 mass%	60	BO/PMMA, 47.00 mass%	87

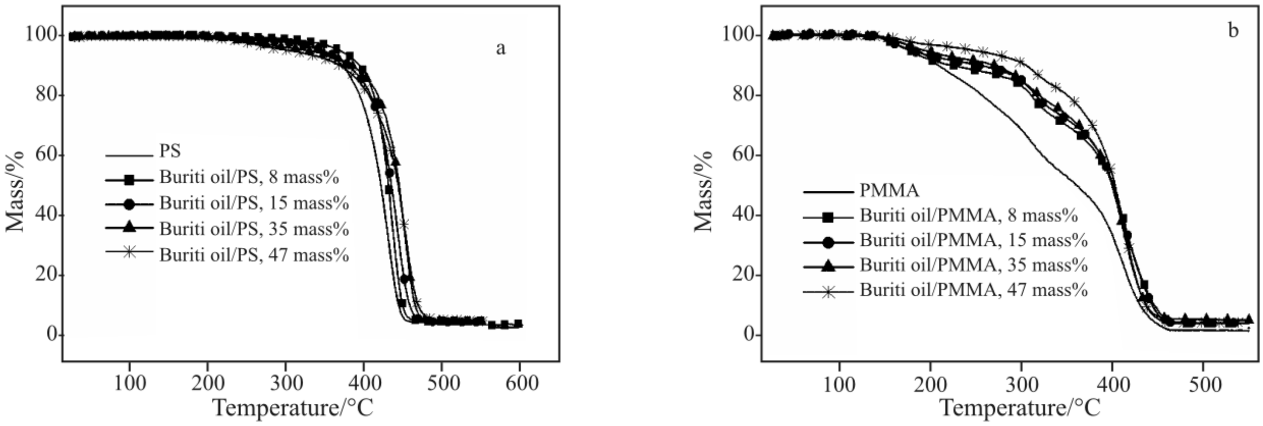

Fig. 5 TG plots of a – PS and Buriti oil/PS mixtures and b – PMMA and Buriti oil/PMMA mixtures

curred since the mass loss decreased even if the T_d values have not increased (Table 3).

This incorporation of the oil contributes to prevent the unzipping process of the polymer main chains and consequently leads to smaller mass loss. The second degradation (T_d2) corresponds to the action of radicals generated at terminal double bonds which were formed by disproportionation process, i.e. involves the attack to the terminal double bonds by radicals [13]. This process leads to the random chain scission that occurs near 410°C. BO does not promote a significant increase in T_d values of second or third decomposition steps but reduced the second mass loss as well as impelled the mass loss of the third stage. In other words, the oil increased the degradation rate in this last step. The intensity of this process is also proportional to the amount of BO in the matrix (Table 3).

Figure 6 shows the TMA plots in the penetration mode for PMMA and BO/PMMA mixtures submitted to 10 and 100 mN loads. The T_s values are listed in Table 4 and reveal that the incorporation of BO on the PMMA matrices does not promote significant change in the thermal mechanical properties of the mixtures, in this case resistance to penetration. In the experiment carried out with application of the 10 mN load it was observed that the softening of the bulk PMMA happens abruptly while in the blends it occurred in a milder way. Furthermore, the hybrid material BO/PMMA showed more resistance to penetration than the PMMA, even without a significant increase in the T_s. When the higher load was employed, an opposite behavior was noticed: almost all blends presented an irregular decrease in the T_s values compared to that of pure PMMA (66°C). As shown by DSC and SEM results the materials seem to be phase separated. Despite of this, London forces promote large cohesion between the distinct phases and thus higher resistance to penetration in the case of the 10 mN load. However, these forces are not strong enough to maintain cohesion in the case of higher (100 mN) load.

This observation can be also explained by the two opposite behaviors recorded by TMA for the BO/PS blends (Fig. 6): softening occurs at lower temperatures; each time the oil content increases when the lower load was applied; but the inverse situation is observed for the 100 mN load (Table 4).

Table 3 Data of decomposition temperature (T_d) and percentual mass loss

Sample	T_d1/°C	Mass loss/%	T_d2/°C	Mass loss/%	T_d3/°C	Mass loss/%
PS			–	–	429	97
BO/PS, 8.00 mass%			–	–	434	97
BO/PS, 15.00 mass%			–	–	442	98
BO/PS, 35.00 mass%			–	–	450	92
BO/PS, 47.00 mass%					452	90
PMMA	197	14	306	30	412	56
BO/PMMA, 8.00 mass%	180	4	311	15	414	68
BO/PMMA, 15.00 mass%	145	7	314	18	413	73
BO/PMMA, 35.00 mass%	168	6	313	15	413	73
BO/PMMA, 47.00 mass%	171	4	313	10	412	81

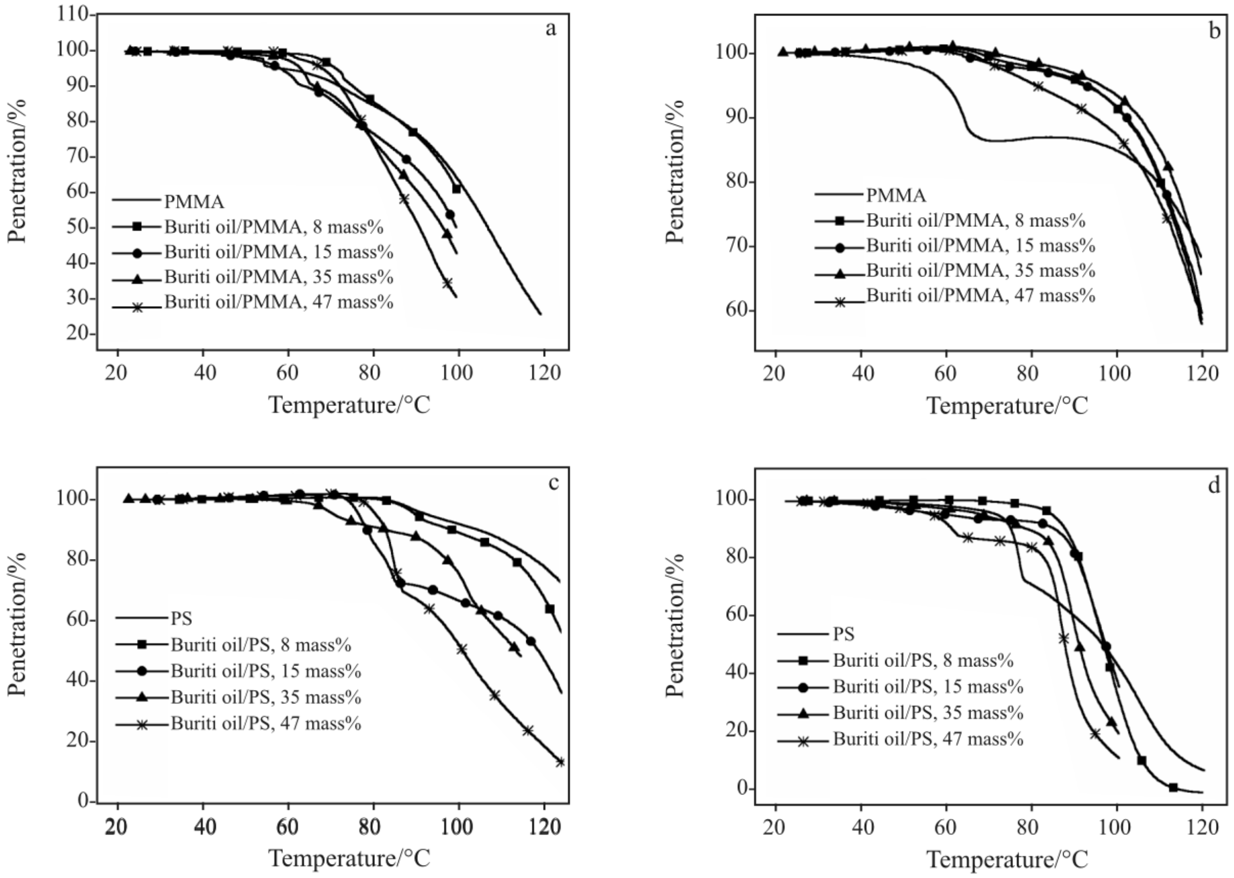

Fig. 6 TMA curves of PMMA and Buriti oil/PMMA mixtures: a – load 10 mN, b – 100 mN, and PS and Buriti oil/PS mixtures: c – load 10 mN, d – 100 mN (penetration mode)

Table 4 Softening temperature (T_s) of the materials at different loadings

Sample	T_s/°C	
	10 mN	100 mN
PMMA	60	66
BO/PMMA, 8.00 mass%	65	66
BO/PMMA, 15.00 mass%	61	55
BO/PMMA, 35.00 mass%	62	62
BO/PMMA, 47.00 mass%	64	59
PS	79	74
BO/PS, 8.00 mass%	82	86
BO/PS, 15.00 mass%	71	85
BO/PS, 35.00 mass%	64	83
BO/PS, 47.00 mass%	73	82

Conclusions

This work was a preliminary study on the thermal and structural behavior of Buriti oil mixed with PS and PMMA. All the mixtures exhibited lower T_g compared to the value for the bulk polymers, showing that the oil lubricates the polymeric chains even if this plastifying action has not been so pronounced. BO does not modify the degradation mechanisms of the polymers but the oil itself is able to increase the degradation temperature of PS up to 22°C and to result changes in the mass loss of PMMA. DSC data and SEM results show that most mixtures are heterogeneous ones. However, the resistance of the substances to penetration was not harmed.

Acknowledgements

The authors are grateful to financial support from CNPq, FAP-DF and FINATEC Brazilian Agencies.

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Received: May 8, 2007
Accepted: November 16, 2007

DOI: 10.1007/s10973-007-8564-z