

Properties of polyurethane elastomers and composites by thermal analysis

C.G. Mothé^{*,1}, C.R. de Araújo

*Escola de Química/DPO, Universidade Federal do Rio de Janeiro, Centro de Tecnologia-Bloco E,
CEP 21949-900, Rio de Janeiro, Brazil*

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Abstract

Polyurethane elastomers based on castor oil or polybutadiene liquid hidroxyol (PBLH), as well as polyurethane composites reinforced with coir or sisal fibers at different proportions: 5, 10 and 20% w/w were prepared. The thermal behavior of the samples was analyzed by thermogravimetry (TG/DTG). TG/DTG curves showed two decomposition stages, except samples from castor oil with three decomposition stages (Tonset 257°C). The PU from PBLH presented a principal degradation at around 400°C, but with 15% weight loss at 250°C and the composites exhibited first decomposition stage at around 290°C. MDSC thermal profiles for PBLH PU presented one transition, occurring at the glass transition temperature (T_g) 73.8°C, two transitions in castor oil PU T_g : -1.6 and 62.7°C, and three transitions for composites from sisal T_g : -52.9°C, 66.7 and 122°C. These transitions suggest soft and hard segments. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of renewable raw material resources has attracted the attention of many researchers [1–3], because of their potential to substitute petrochemical derivatives. The use of natural fibers like coir, sisal, bagasse of sugar cane, jute, ramie and pineapple-leaf reinforced plastics (FRP) can lead to materials with properties such as: thermal and impact resistance, low density, flexibility, biodegradability and low cost. However, properties of the composites depend on many factors like fiber-matrix adhesion, volume frac-

tion of fiber, fiber orientation and polymer used [4]. On the other hand, synthetic fibers such as: glass, carbon, boron, nylon and Kevlar are generally used to make composite materials for specific purposes with high strength properties which do not deteriorate appreciably with time, but they are expensive and are non-renewable resources. Coir is a lignocellulosic fiber obtained from the mesocarp of coconut, the fruit of coconut tree, *Cocos nucifera*, cultivated extensively in the tropics. India and Sri Lanka are the world's largest producers [5]. Sisal fiber is also a lignocellulosic extracted from the plant *Agave Veracruz* and is available in quantity in the southern parts of India. In the present study, we report on some thermal properties of polyurethanes (PU) using castor oil, *Ricinus Communis*, or polybutadiene liquid hidroxyol (PBLH) and PU composites reinforced with coir or sisal fibers.

* Corresponding author. Fax: +55-21-5904991.
E-mail addresses: sm@nysaes.comell.edu, cheila@h2o.eq.ufrj.br
(C.G. Mothé)

¹ Bolsista da CAPES-Brasília/Brasil

2. Experimental

2.1. Materials

Refined, castor oil was used without any further purification. Its characteristic values such as saponification number (175 mg KOH/g), molecular weight (956), were determined by ASTM D1957-63 and ricinoleic acid (86%) by gas chromatography on a Hewlett Packard, model 5890 A.

Polybutadiene liquid hydroxyl (PBLH), molecular weight (3000), was supplied by Petroflex SA, Rio de Janeiro, Brazil.

Coir and sisal fibers were supplied by Mercedes-Benz. The coir fiber 6–20 mm was treated with a 5% sodium solution for 48 h, washed with water and dried in an air oven.

2.2. Polyurethane synthesis

Castor oil or PBLH was reacted with toluene 2,4-diisocyanate (TDI) and dibutyl tin dilaurate as catalyst to maintain the NCO/OH ratio at 1.0, 1.5 and 2.0. The reaction (one-shot polymerization) took place at room temperature until a visible viscosity change occurred, when necessary, an amount of MEK was introduced to assure an adequate viscosity to the solution and obtain the elastomers.

2.3. Composites

The commercial polyurethane pellets from Cofade Ltda and coir or sisal fibers with different proportion such as: 5, 10 and 20% w/w, were prepared by melt mixing, in a Haake rheometer, at 100°C, 60 rpm for 15 min. These samples were cured in a carver press at 140°C and 10,000 lb/in².

2.4. TG/DTG measurements

The experiments were carried out on a TA instruments SDT 2960, at a heating rate of 10°C/min in nitrogen atmosphere and in the temperature range 0–800°C

2.5. MDSC measurements

The thermal transitions of the composites with 20% w/w were determined with a modulated differential

scanning calorimeter, model 157 TA. Samples containing 8–9 mg of material, were heated at a heating rate of 5°C/min from –100 to 200°C.

2.6. Microscopy measurements

The tensile fracture surfaces of the composites were examined under a scanning electron microscope (SEM), Jeol model JSM 5300.

3. Results and discussion

Polyurethanes (PU) can be prepared by a variety of methods. There are advantages and disadvantages to each method. The one-shot polymerization results in a more random block polymer and the prepolymer method is a two-step process which gives less random and more block polymers [6]. These polyurethanes consist of alternating segments of hard and soft blocks. The hard segments are formed by extension of an aromatic diisocyanate and the soft segments are polyethers or polyesters [7]. The typical polyurethane is extensively hydrogen bonded, the donor being the NH group of the urethane linkage. The hydrogen-bond acceptor may be either the hard segment or the soft segment. Fig. 1 shows thermogravimetric (TG) curves for PU elastomers (NCO/OH: 2.0) and composites (20% w/w fiber). Two decomposition stages can be seen, except in samples from castor oil that had three decomposition stages (Tonset 257°C) and a residue of 5%. The PU from PBLH presented a principal degradation at around 400°C, but with 15% weight loss at 250°C and without residue. The first weight loss for PU commercial sample occurred at around 300°C and a residue of 12% and the composites exhibited similar thermal behavior [8–9], with first decomposition stage at around 290°C.

Derivative thermogravimetric (DTG) curves in Fig. 2 depict a minor thermal stability for PU from castor oil, major in PU from PBLH and a slight decrease in thermal stability of the composites, which agree with the TG response.

MDSC thermograms (Fig. 3) exhibited one transition for PBLH PU with change of the base line, occurring at the glass transition temperature (T_g)

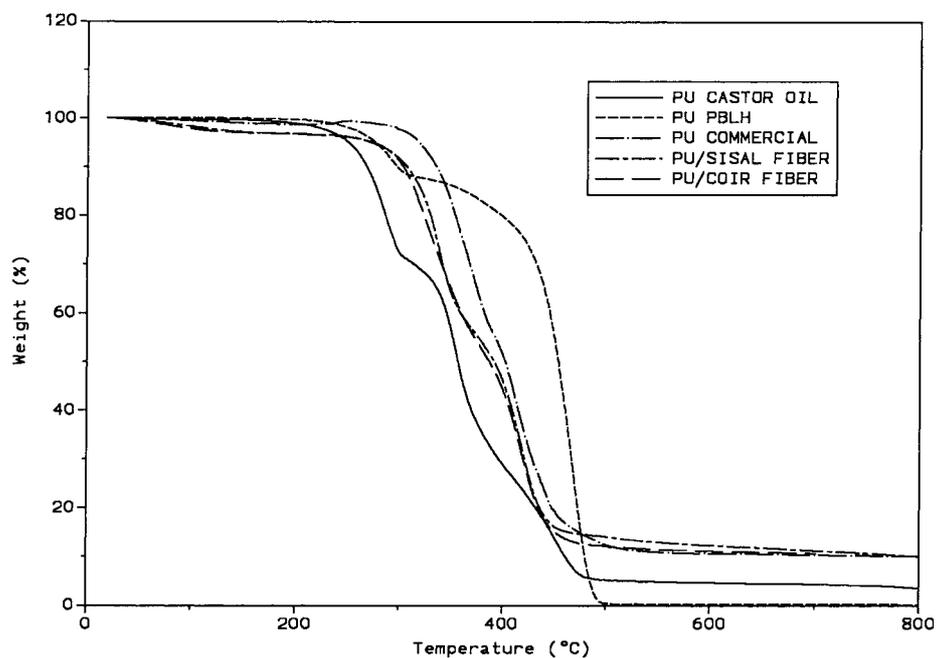


Fig. 1. Thermogravimetric curves for PU elastomers and PU composites.

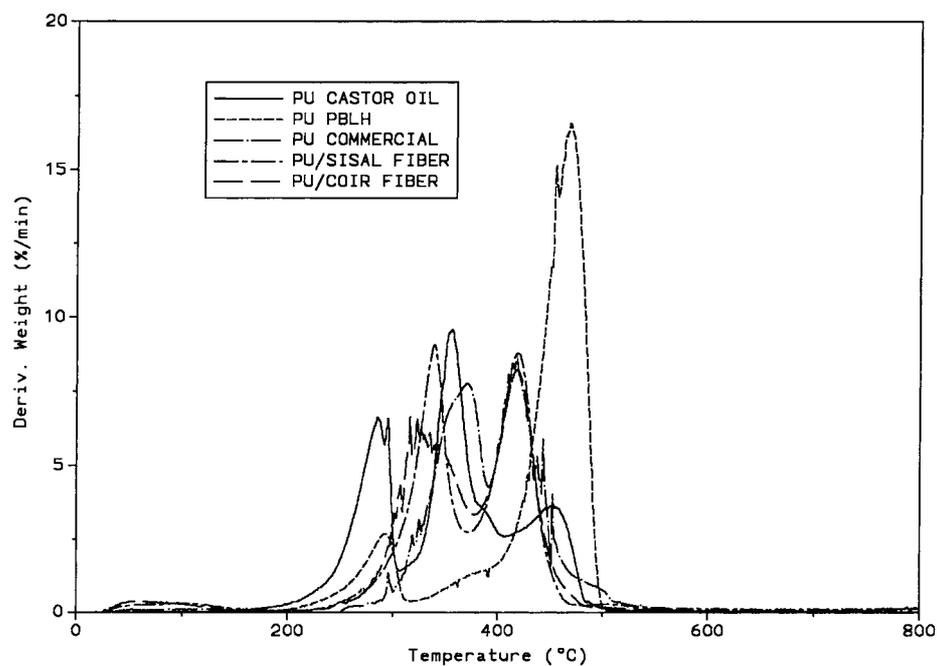


Fig. 2. Derivative thermogravimetric curves for PU elastomers and PU composites.

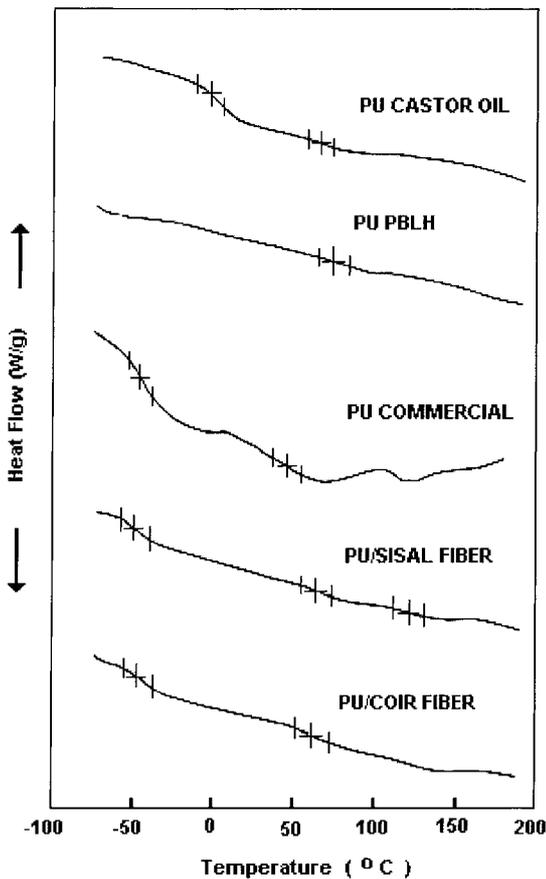
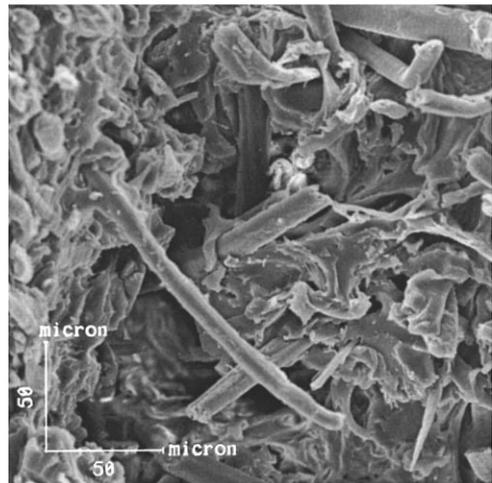


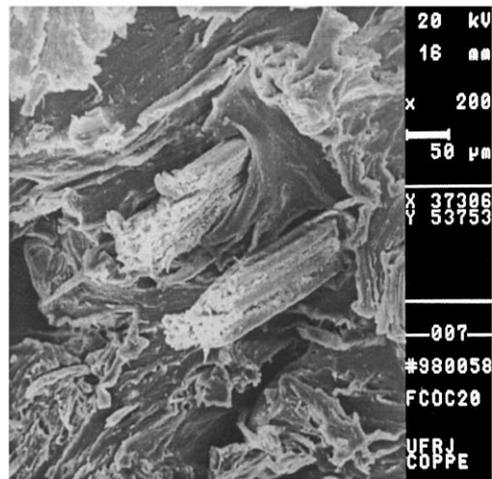
Fig. 3. MDSC curves for PU elastomers and PU composites.

73.8°C. Two transitions in castor oil PU T_g : -1.6°C and 62.7°C ; coir fiber PU T_g : -46.2°C and 61.1°C . Three transitions in commercial PU T_g : -47.5°C , 46°C and 105°C ; sisal fiber PU T_g : -52.9°C , 66.7°C and 122°C . These transitions suggest soft and hard segments. The use of PBLH showed predominant hard segments and use of castor oil shifted the main transition region of the soft phase to higher temperature [1], T_g increase, the functionality of castor oil resulted in the crosslinking of the soft segments. The composites from coir fiber showed a slight increase (soft phase) at glass transition temperature.

SEM micrographs of the fracture region from tensile tests are shown in Fig. 4(a) for PU composite with 20% w/w of sisal fiber and (b) 20% w/w of coir fiber.



(a)



(b)

Fig. 4. SEM analysis of fracture region from tensile tests: (a) PU/sisal fiber ($\times 500$) and PU/coir fiber ($\times 200$).

The fracture surface exhibits fibers pullout for both composites.

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