

# Mechanical and Thermal Properties of Polyurethane Elastomers Based on Hydroxyl-Terminated Polybutadienes and Biopitch

Renata Costa Silva Araújo, Vânia Márcia Duarte Pasa

Departamento de Química, Universidade Federal de Minas Gerais, Avenue Antônio Carlos, 6627, Belo Horizonte, Brazil

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**ABSTRACT:** Biopitch is a renewable source of polyol obtained from *Eucalyptus* tar distillation, which was studied as an active component of polyurethane (PU). The polymerization occurred in one step, with a mixture of biopitch and hydroxyl-terminated polybutadiene polyols reacted with 4-4'-diphenyl methane diisocyanate in the presence of dibutyltin dilaurate. Solid-state  $^{13}\text{C}$ -NMR, IR spectroscopy, elemental analysis, and thermal analysis [thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)] were used to characterize the biopitch. The biopitch sample showed an aromatic and oxygenated structure with great thermal stability at high temperatures. Multiphase PUs

were synthesized and characterized by IR spectroscopy (attenuated total reflectance), elemental analysis, thermal analysis (TGA and DSC), mechanical assays (tensile strength, elongation at break, toughness, hardness, and resilience), and water absorption resistance (ASTM D 570-81). In a comparative study of the synthesized elastomers, biopitch content increased tensile strength and hardness and decreased thermal stability, elongation at break, and water absorption. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 759–766, 2003

**Key words:** polyurethanes; elastomers; thermal properties; mechanical properties

## INTRODUCTION

In the recent years, renewable resources have attracted the attention of many researchers from all over the world for their use as potential substitutes for petrochemicals. The focus has been mainly on the development of new materials from forest products, with consideration for their positive impact on the reduction of the greenhouse effect. Brazil has an important iron-making industry, which consumes about 6 million tons/year of charcoal and uses this raw material as a thermoreducer, mainly in pig-iron production. The vapors generated during *Eucalyptus* carbonization are washed and condensed to recover about 140 kg of wood tar per ton of charcoal.<sup>1</sup> The biopitches are obtained as a tar distillation residue, which can be considered a natural polyol, corresponding to 50% *Eucalyptus* wood tar. When planted forests are considered, the Brazilian biopitch production potential is about 200,000 tons/year, high enough to stimulate the production of different polymeric materials with this low-cost raw material.<sup>2</sup>

Polyurethanes (PUs) are an important class of synthetic polymers, contributing with about 8.5 mil-

lion tons/year of the world market.<sup>3</sup> These extremely versatile polymers can be synthesized basically by the reaction of polyols and isocyanates. Generally, polyester and polyether polyols are the most used in the synthesis of PUs, but polycarbonates, polythioethers, polyaminoethers, polyacetals, polysulfonates, polysiloxanes, and hydroxyl-terminated polybutadienes (HTPBs), among others, have also been used.<sup>4</sup>

Many studies are under way to develop PUs with polyols from renewable sources, mainly lignin.<sup>5,6</sup> This starting material is used not only for its natural abundance and renewability but also because it is one of the largest low-value industrial byproducts. Lignin is viewed as an inexpensive, inert filler and extender. Generally, the incorporation of lignin as an active component is limited because of its heterogeneous and complex structure, its poor solubility, and poorly defined glass transition.<sup>7</sup> These characteristics make necessary prior treatment to improve access to hydroxyl groups. Sarkar and Adhikari carried out the syntheses of PU with HTPB and lignin, but its high hydroxyl content limited its loading into the PU structure.<sup>8</sup>

Studies of biopitch characterization have shown the chemical similarity between pitch and lignin. Both preserve guaiacyl and siringyl units, even after carbonization.<sup>9</sup> Biopitch has a complex chemical structure like that of a fragmented lignin and can be

Correspondence to: V. M. D. Pasa (vanya@dedalus.lcc.ufmg.br).

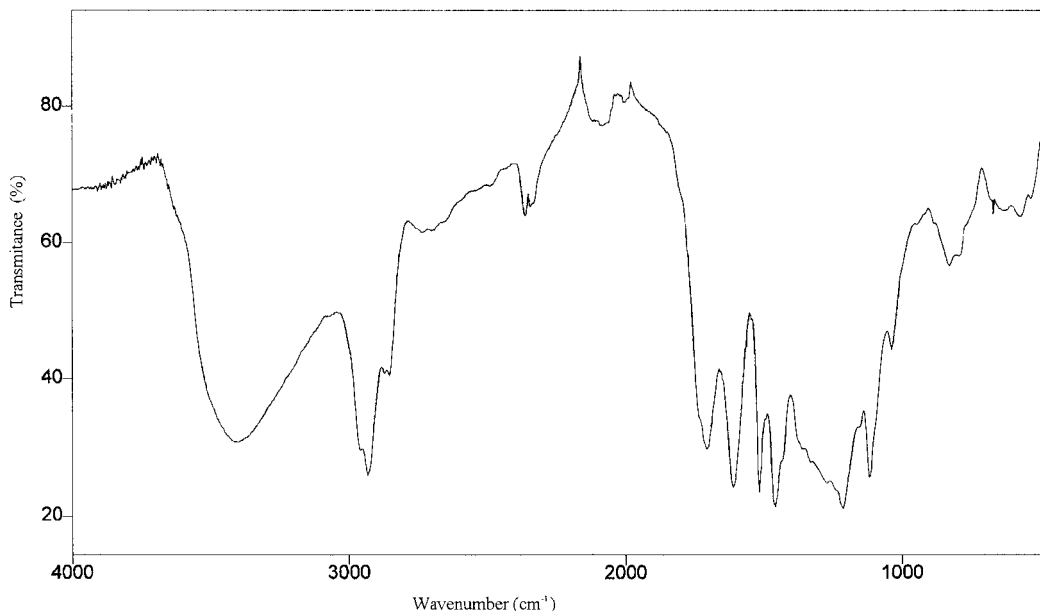


Figure 1 Biopitch IR absorption spectrum (KBr pellets).

called *fusible lignin* because of its thermoplastic behavior, which affords more solubility, mobility, and homogeneity during polymerization as compared to lignin.<sup>10</sup> These features have encouraged the use of biopitch in PUs as an active component.

## EXPERIMENTAL

### Materials

The reagents used were

1. The Biopitch sample, which was obtained as a solid residue during the vacuum distillation process of *Eucalyptus* tar, in a pilot plant unit (yield 50% w/w). The tar was recovered by an industrial masonry kiln, from Acesita (Timóteo).
2. HTPB (Petroflex, Rio de Janeiro, Brazil).
3. Polymeric 4-4'-diphenyl methane diisocyanate (MDI) system (VL R 20 BR; Bayer).

### Methods

Determination of hydroxyl-group content in biopitch: acetylation

Biopitch (1.0 g) was added to a mixture of acetic anhydride (5.0 mL) and pyridine (5.0 mL). The reaction mixture was stirred and refluxed for 100 h. The mixture was poured into a beaker containing ice. The acetylated pitch was precipitated and filtered. The product was dried and stored in a vacuum desiccator. Afterward, titration was carried out with NaOH (1.69 equiv g/L) to determine hydroxyl content.

### Preparation of PU films

PU films were prepared in a tetrahydrofuran (THF) solution by biopitch polymerization with MDI, HTPB, and dibutyltin dilaurate as a catalyst in one step. The NCO/OH ratio was 0.8. The biopitch proportions to HTPB in elastomer synthesis assumed different values: 0, 10, 20, 30, 40, and 100%. The mixture was poured and cured under vacuum for 3 h. Subsequently, the cure was completed in an overnight heat treatment at 80°C.

### Characterization

*Elemental analysis.* The samples were analyzed on a PerkinElmer 240B to determine %C, %H, %N, and %O by difference. The O/C ratio was calculated and related to the degree of oxygenation of biopitch and PU films.

*Solid-state <sup>13</sup>C-NMR.* Spectra were taken on a VARIAN INOVA-300 with probe RT CP/MAS. NMR analysis was carried out for the biopitch sample used.

*IR analysis.* The biopitch IR absorption spectra was assessed with a PerkinElmer 283B spectrophotometer with KBr pellets, and the concentrations used were 1 and 3%. The IR spectra for the PU films were carried out on a Fourier transform infrared spectrometer (PerkinElmer 1000) by attenuated total reflectance (ATR).

*Thermogravimetric analysis (TGA).* A Shimadzu TGA apparatus was used for thermogravimetry. The measurements were carried out with approximately 6 mg of sample at a heating rate of 10°C/min and a flow

TABLE I  
Solid-State  $^{13}\text{C}$ -NMR Analysis of the Biopitch used to Prepare PUs

Region	Group	Functionality	Chemical shift (ppm)	Carbon content (%)
	9		14	7.9
3	8		20	4.1
	7		29-50	11.8
	6		50-70	3.5
2	5		110-115	8.7
	4		115-140	30.2
	3		140-160	27.0
1	2		160-185	
	1		190-230	6.8

rate of 150 mL/min in both nitrogen and air atmospheres.

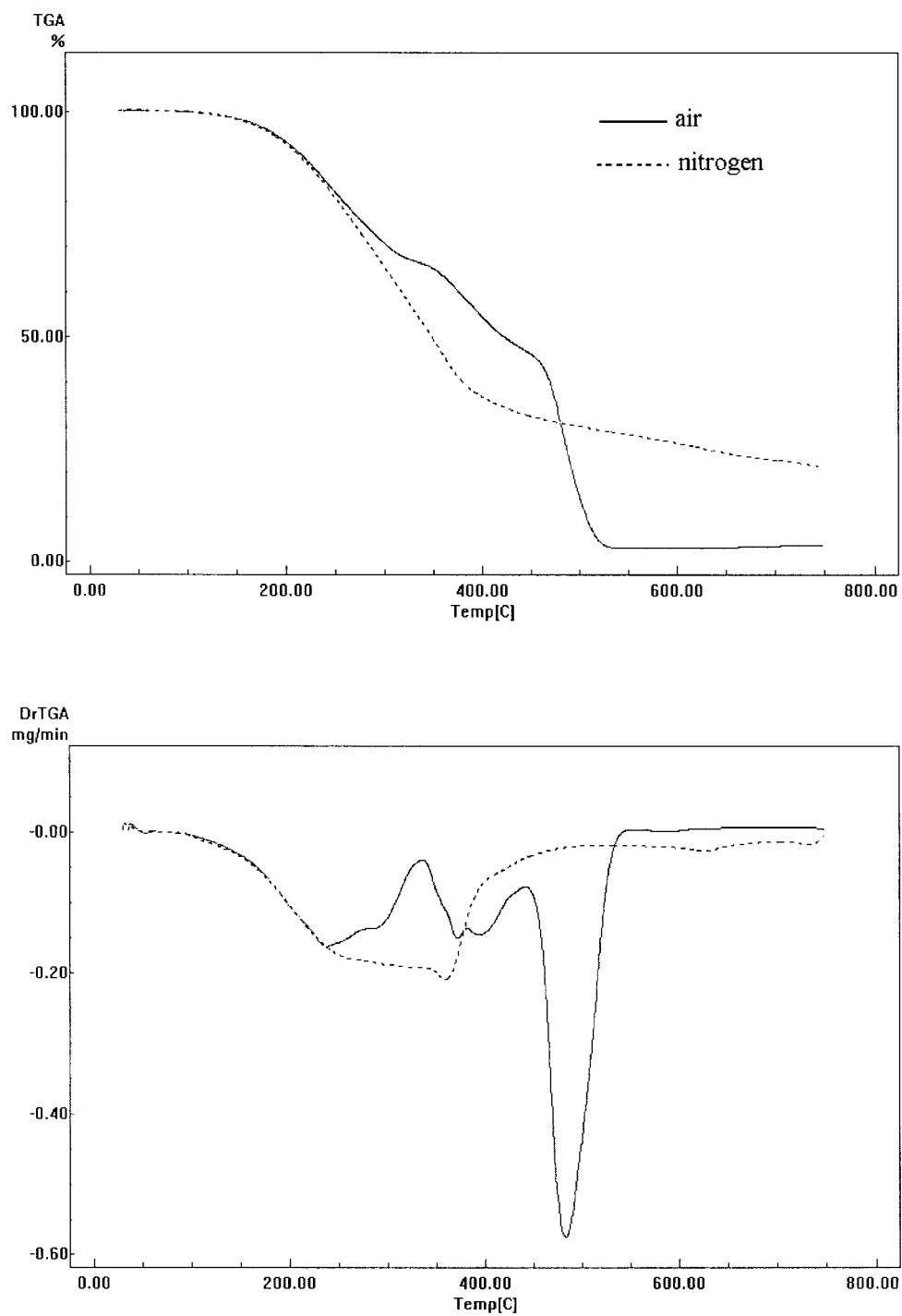
*Differential scanning calorimetry (DSC).* DSC was performed with a Shimadzu DSC 50 apparatus, and the glass-transition temperature ( $T_g$ ) was defined as the midpoint of change in heat capacity occurring over the transition. The samples were first scanned at 150°C; thereafter, they were cooled, and a second scan was

recorded.  $T_g$  was determined under a helium atmosphere at heating rate of 20°C/min.

*Mechanical properties.* Tensile tests of PUs were performed at 23°C with an Instron 4200 machine with standard method ASTM D 412-87. The crosshead speed and distances were 500 mm/min and 10 mm, respectively. The Shore A hardness (ASTM D 2240-86) and resilience were obtained also.

**TABLE II**  
**Elemental Analysis (for Pitch and PUs) and Water Absorption (for PUs)**

Sample	%C	%H	%N	%O	H/C	O/C ( $\times 10^2$ )	Water absorption (%)
10%	83.5	10.2	1.2	5.1	1.5	4.6	0.02
20%	81.9	10.2	1.5	6.3	1.5	5.8	0.09
30%	81.4	9.9	1.5	7.1	1.5	6.6	0.07
40%	81.2	9.8	1.5	7.5	1.4	6.9	0.25
Biopitch	69.9	6.2	0.0	23.8	1.1	25.0	—



**Figure 2** TGA and DTG curves for biopitch in air and nitrogen atmospheres.

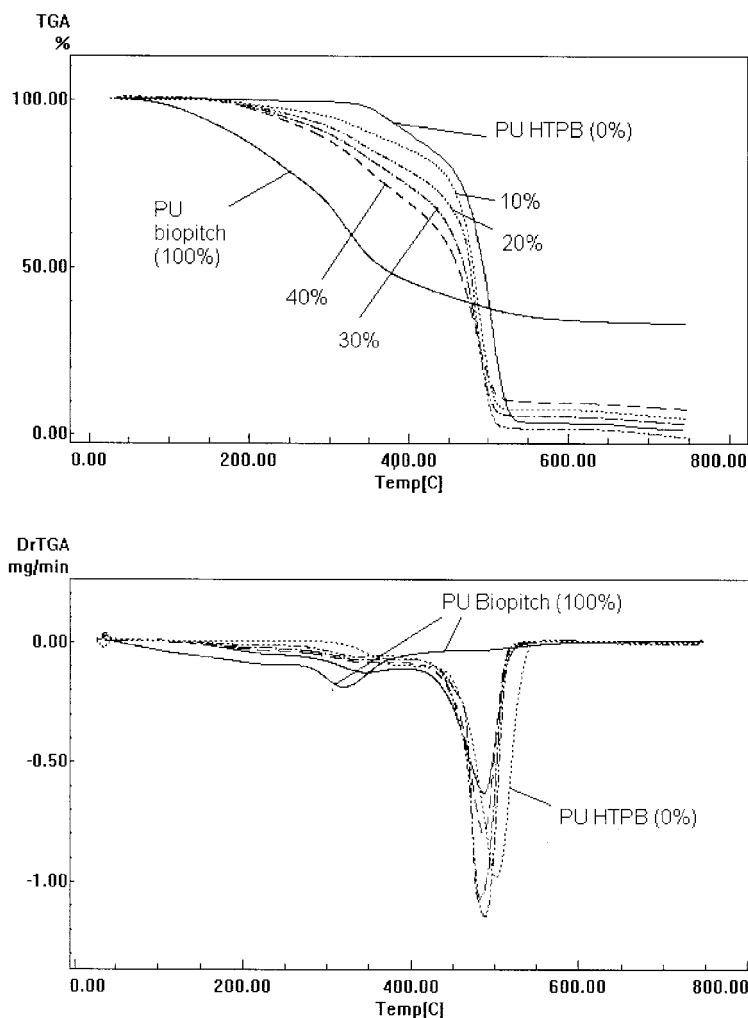


Figure 4 TGA and DTG curves for pitch and PUs based on biopitch in a nitrogen atmosphere.

*Resistance to water absorption.* The tests of water absorption were carried out according to ASTM D 570-81 for 24 h in triplicate to evaluate the impermeability capacity of PUs based in biopitch and HTPB.

## RESULTS AND DISCUSSION

### Biopitch

Biopitch was characterized in this investigation to confirm its polyol structure and to contribute to the state of the art of this oligomer. The acetylation procedure showed that biopitch had 7% (153 mg of KOH/g) OH content. IR spectroscopy of pitch (Fig. 1) and solid-state  $^{13}\text{C}$ -NMR analysis (Table I) showed the different chemical groups that constituted the biopitch macromolecular structure. As shown in the  $^{13}\text{C}$ -NMR results, the hydroxyl groups that constituted PU were basically phenolic hydroxyls. In both analyses, it was possible to verify the high aromatic content of biopitch, and in the IR spectra, its characteristic hydroxyl absorption ( $3300\text{ cm}^{-1}$ ) was evident. Pitch presented

mainly absorption relative to the carbonyl group and ether bonds (at  $1705$  and  $1100\text{ cm}^{-1}$ , respectively), which were attributed to guaiacyl and syringyl units.

Investigations of biopitch showed its aromatic nature and its high oxygen content (24%), as seen in Table II. Such results were determined by elemental analysis with O/C and H/C ratios of  $2.5 \times 10^{-1}$  and 1.1, respectively. The biopitch structure was different when compared to those of coal tar pitch, which has O/C and H/C ratios of  $0.6 \times 10^{-3}$  and  $8 \times 10^{-3}$ , respectively, and petroleum pitch, which has O/C and H/C ratios of  $0.8 \times 10^{-3}$  and  $4 \times 10^{-3}$  respectively.<sup>11</sup>

The biopitch TGA and differential thermogravimetry (DTG) curves (see Fig. 2) showed no difference until weight loss reached approximately 10% in air and nitrogen atmospheres. However, biopitch degradation in nitrogen occurred rapidly after this point. In an air atmosphere, degradation mechanisms were different, as observed by the shoulder in the TGA curve and by an increase in thermal stability. The thermal analyses of lignin and PUs based on lignin available in

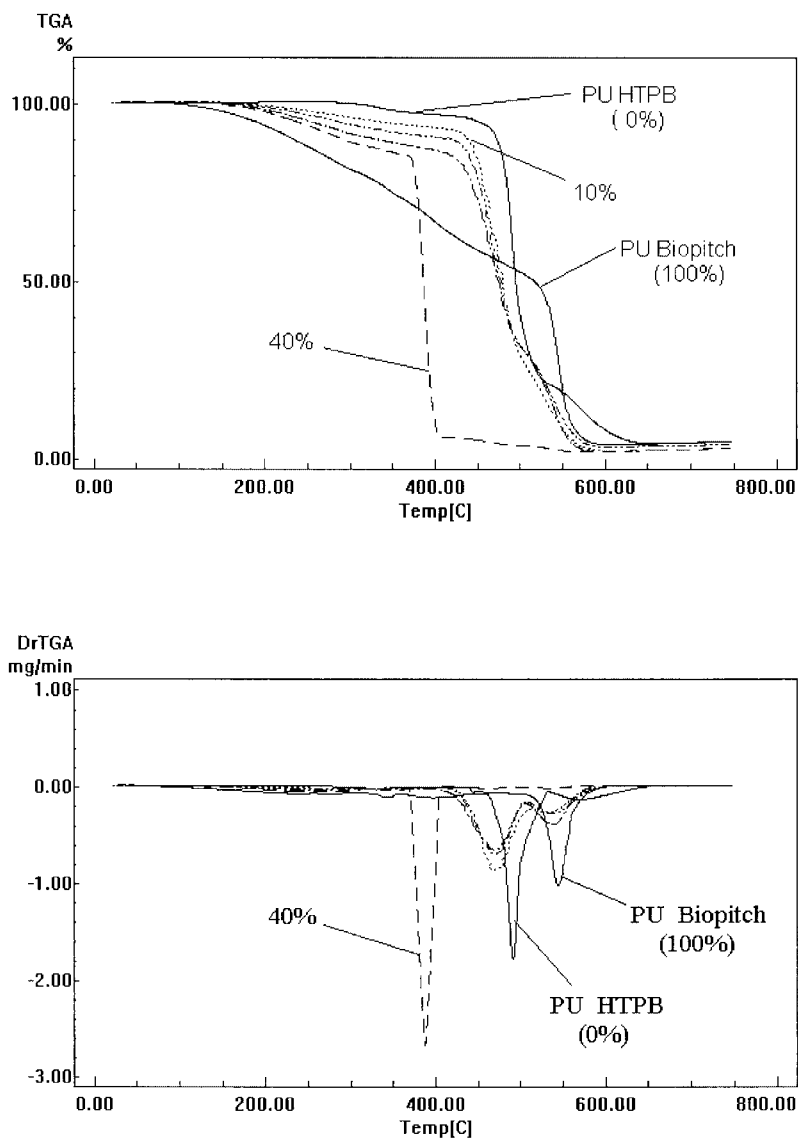


Figure 5 TGA and DTG curves for pitch and PUs based on biopitch in an air atmosphere.

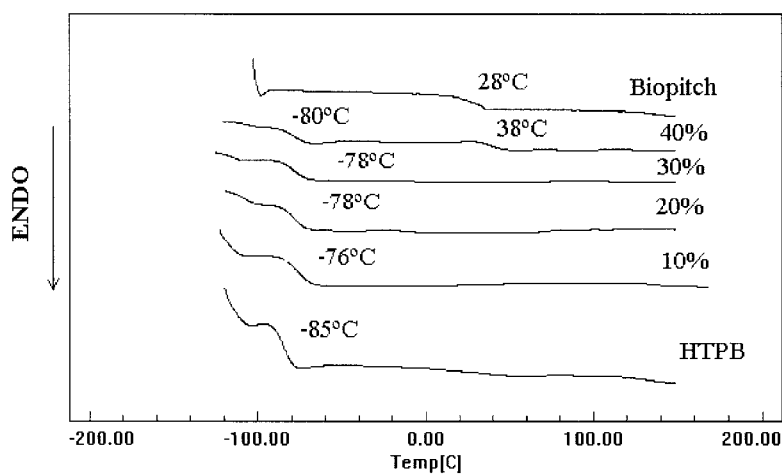


Figure 6 DSC curves for PUs and polyols used in the synthesis.

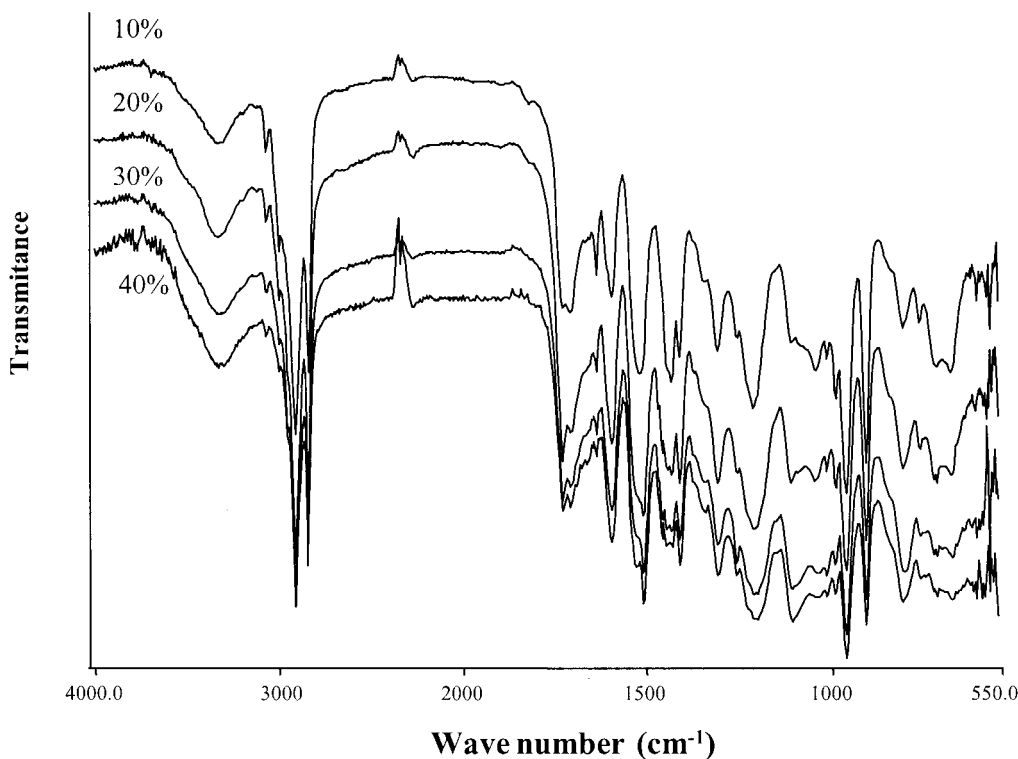


Figure 3 IR (ATR) spectra for PUs (10, 20, 30, and 40% of biopitch content).

the literature show the same behavior with an increase of stability in air atmospheres, mainly due to the aromatic character and condensation reactions under the participation of radicals formed by the reaction of lignin with oxygen air.<sup>12</sup>

### PUs

The synthesized elastomers presented a good aspect, although low homogeneity was observed between the polyols, which was minimized by previous dissolution in THF. The polarity difference between both polyols used caused the multiphasic aspects in the PU elastomers.

The results of elemental analysis of PUs showed an increase in the oxygen content with the addition of biopitch, as expected. Table II shows the capacity of biopitch to resist water absorption. Water absorption for the PUs synthesized was very low even when the biopitch content increased. These results show that the hydrophobic characteristic of HTPB prevailed over the addition of oxygenated material (biopitch). The results of this study suggest that these elastomers can be used in the manufacture of waterproof materials.

Figure 3 shows that the IR spectra of PUs, obtained by Fourier transform infrared spectroscopy-ATR, confirmed the formation of PU ( $\text{—NHCOO—}$ ) due to the presence of the carbonyl group ( $\text{C=O}$ ) at  $1730\text{ cm}^{-1}$ . The disappearance of the characteristic absorption of the NCO stretching at  $2275\text{ cm}^{-1}$  showed that all of

the MDI reacted, forming urethanic bonds with polyols. Other absorption bands in the spectrum were relative to the polyol groups.

The thermal stability of PUs was carried out in air and nitrogen and showed two completely different behaviors. TGA and DTG curves were analyzed comparatively (Figs. 4 and 5). In the nitrogen atmosphere, a decrease was observed in PU's  $T_{\text{onset}}$  with pitch addition. Material degradation occurred mainly in two events, as shown in the DTG curves. These PU degradations occurred because of the segmented structure characteristic of these materials. The first event ( $300^{\circ}\text{C}$ ) was attributed to the hard segments in which the biopitch was inserted, whereas the second one ( $480\text{--}520^{\circ}\text{C}$ ) was related to the soft segments formed by HTPB. The lower thermal stability of hard segments was corroborated by studies on the pyrolysis of PUs found in the literature.<sup>13</sup> Also, in the thermal analysis (TGA), a quantitative relationship was observed between the biopitch used in formulations and the degradation event of hard segments and the residual mass, suggesting that biopitch was located at this stage of degradation.

The results of TGA in the air atmosphere (Fig. 5) show that PUs synthesized with HTPB and biopitch presented a decrease in thermal stability with the addition of biopitch in their macromolecular structures. Their thermal degradation occurred in two different events, as shown in the DTG curves. The PUs based only by HTPB (0%) or biopitch (100%) showed a single

**TABLE III**  
**Mechanical Properties Obtained for Elastomers of PUs Based on Biopitch**

Biopitch content (%)	Tensile strength (MPa)	Ultimate strength (MPa)	Elongation at break (%)	Resilience (%)	Toughness (MPa)	Shore A hardness
10	14.5	1.8	193.0	36.0	1.7	34.0
20	23.6	2.6	102.0	34.0	1.4	56.0
30	32.3	4.6	116.0	33.0	2.2	63.0
40	55.0	6.8	71.0	32.0	3.3	78.0

event of degradation in the air atmosphere. The same occurred with 40% of biopitch content, which suggests that there was a limit content of the mixture of biopitch and HTPB in the PU system. In addition, there was a strong decrease in PU thermal stability. The PU biopitch (100%) showed special thermal stability in air at higher temperatures (550°C) after its weight loss reached 50%. This behavior was similar to PUs based on lignin, which have a retarded thermal degradation, as reported in the literature.<sup>12</sup> In the air atmosphere, the event regarding hard segments seemed occur at higher temperature (550°C) in contrast, which happened in the N<sub>2</sub> atmosphere. It could be explained by the aromatic character of biopitch, the main component of hard segments. During the thermal process, the aromatic rings generates a carbon layer, which retards the degradation of material.

The DSC curves were obtained in a second scan (Fig. 6) and showed slight changes in  $T_g$ 's observed for PUs with biopitch addition.  $T_g$ 's did not show great variations with pitch addition because of the multiphases present in the materials. No melting endotherm appeared in the first or second scans for any PU samples based on biopitch, which indicated the absence of crystallinity in these materials.  $T_g$ 's under room temperature referred to the soft segments present in PUs and were attributed to HTPB. The curve of the sample with 40% of biopitch content showed a second  $T_g$  at 38°C; possibly, this could be relative to the hard segments, into which the pitch was inserted. As shown in Figure 6, the biopitch  $T_g$  occurred at 28°C. This second  $T_g$  (38°C) was higher than the  $T_g$  of biopitch, probably because of the lower mobility of their aromatic rings in PU structures. Others samples did not show this second  $T_g$ , probably because of the small quantity of biopitch used, which led to a better homogeneity of the polymeric systems.

The tensile properties of PUs were also studied in this investigation as a function of biopitch content. As shown in Table III, the strength increased with biopitch content, whereas the flexibility was gradually lost. This could be attributed to the introduction of more aromatic rings into the system, which led to an increase in chain stiffness. The toughness increased as biopitch content rose. Although resilience fell slightly with the increase in biopitch content, hardness showed a large rise.

## CONCLUSIONS

It was possible to obtain polyurethanic elastomers starting from mixtures of biopitch and HTPB such as polyols. The thermal stability of the material decreased with the addition of pitch, and it was shown that the biopitch was introduced into the hard segments of PUs. In DSC curves, a variation in  $T_g$  was not observed with biopitch addition, which suggested that these PUs were multiphase materials.

The increase in biopitch content led to increases in tensile strength (14–55 MPa), toughness (1.7–3.3 MPa), and hardness (34–78 Shore A). Resilience varied from 32 to 36% for decreasing pitch contents of 40 to 10%.

These multiphase materials showed low values of water absorption (< 0.3%) and have the potential to be used as waterproof materials.

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