

Composites Based on Eucalyptus Tar Pitch/Castor Oil Polyurethane and Short Sisal Fibers

Breno N. Melo, Vânia M. D. Pasa

Departamento de Química da UFMG, Instituto de Ciências Exatas, Av. Antônio Carlos 6627, Pampulha, CEP 31270-90, Belo Horizonte, Brazil

Received 8 May 2002; accepted 18 November 2002

ABSTRACT: Polymeric materials are being developed with renewable resources to promote industrial progress with environmentally friendly technologies. For this reason, polyurethane samples were prepared with 4,4'-diphenylmethane diisocyanate (NCO/OH = 1), eucalyptus tar pitch (biopitch), castor oil as a polyol, and dibutyltin dilaurate as a catalyst. These materials were reinforced with different contents of short sisal fibers (0, 2.5, 5.0, 7.5, and 10.0%) and were prepared by resin-transfer molding. The composites were characterized by IR absorption spectroscopy, thermal

analysis (thermogravimetry and differential scanning calorimetry), impact resistance, scanning electron microscopy, and water absorption resistance. These materials showed hydrophobic characteristics, despite the addition of sisal fibers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3797–3802, 2003

Key words: polyurethanes; composites; renewable resources; thermal properties; structure-property relations

INTRODUCTION

The use of renewable starting materials in the preparation of polymers has been stimulated over the years by researchers and governmental agencies all over the world as a result of the real need to replace products of petrochemical origins. The use of renewable resources in the production of polymers is nowadays an unquestionable reality that aims to minimize the depletion of the ozone layer and the greenhouse effect provoked by the improper use of fossil starting materials.^{1,2}

Polyurethanes (PUs) constitute a class of polymers with great versatility that permit the manufacturing of products ranging from expanded materials to highly compact materials. Basically generated from the reaction of a polyol and a diisocyanate, they were first developed by Otto Bayer in 1937.³ The use of PUs has been proven viable in composite matrices for their flexibility and abrasion resistance.⁴

Brazil is playing a major role concerning new sustainable-development guidelines in the globalized world, having a significant energy-generation potential from all kinds of biomass.⁵

Eucalyptus tar pitch, produced as a siderurgy charcoal residue mainly in Brazil, is a promising starting material for the production of PUs, including expanded PUs such as rigid, flexible, and semiflexible foams, compact PUs, such as elastomers, and pressed PUs, besides being a potential precursor of carbon fibers.⁶ Biopitch (72% C, 6% H, and 22% O) is a solid residue from eucalyptus tar distillation with low aromaticity (50%) in comparison with fossil tars.⁷ It is similar to lignin, in that it presents guaiacyl and siringyl in its oligomeric structure, but it is a thermoplastic material (softening point = 123°C). It is also a polyol with high hydroxyl contents, ranging from 7 to 15%.^{6,7} Castor oil is a triglyceride derived from the plant *Ricinus communis*, and it presents low hydroxyl contents (5.5%). It is largely used in industries because it allows numberless exclusive modifying reactions.⁸

Sisal fibers, abundant in Brazil, are long (~1.2 m), rigid (~73% cellulose) fibers extracted from the leaves of *Agave sisalana*. In relation to synthetic fibers, vegetal fibers present low density and high hydrophilicity and require treatment before their use in composite materials.⁹

Composite materials are made up of two or more solid phases: fibers (dispersed phase) responsible for stress resistance and a matrix (continuous phase) responsible for stress propagation. The great need for reinforced materials has created a demand for improvements in the mechanical properties of matrices.¹⁰

This work presents the results of the synthesis of composites and the thermal and mechanical characterization of sisal fibers and PUs obtained with vegetal

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

Contract grant sponsor: ACESITA.

Contract grant sponsor: FAPEMIG.

Contract grant sponsor: FIEMG/IEL.

TABLE I
Proportion of Polyols Used to Synthesize the PU Matrix and Fiber Content used for Composite Preparation

Polymeric materials	Proportion of polyols to PU		Fiber content (%)
	Biopitch content (%)	Castor oil content (%)	
PU			
Matrix (0%)	0	100	—
Matrix (25%)	25	75	—
Composite			
C25% (2.5%)	25	75	2.5
C25% (5.0%)	25	75	5.0
C25% (7.5%)	25	75	7.5
C25% (10.0%)	25	75	10.0

tar polyols and castor oil, 4,4'-diphenylmethane diisocyanate (MDI), and dibutyltin dilaurate as a catalyst.

EXPERIMENTAL

Preparation of the sisal fibers

The sisal fibers were pretreated with a 5% NaOH solution under mechanical stirring followed by washing with fresh water. During the process, the washing solution basicity was checked with phenolphthalein and neutralized with an HCl bath at 0.05 equiv/L; the fibers were washed again with water. Next, the fibers were air-dried at 105°C for 48 h, that is, until the weight was constant.

Matrix synthesis

Dosing of the hydroxyl polyols

The determination of the functionality of wood tar pitch was made by acetylation (acetic anhydride/pyridine) and countertitration with NaOH solutions. The hydroxyl content was determined by the difference in the amounts of NaOH spent with the blank system and those containing biopitch.

Castor oil had its hydroxyls dosed according to ASTM D 1957-63.

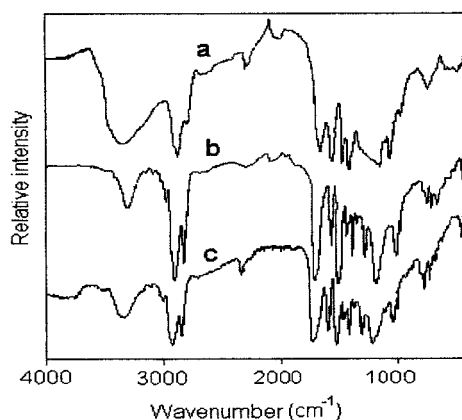


Figure 1 IR spectra of (a) biopitch, (b) Matrix (0%), and (c) Matrix (25%).

Composite synthesis

PU matrices were synthesized in a single-step process. Predried wood tar pitch and castor oil were used along with MDI (NCO/OH = 1) and dibutyltin dilaurate as a catalyst. The mixture was reacted under mechanical stirring until a highly viscous mass with a homogeneous aspect was obtained.

Sisal fibers were randomly placed in a mold. The PU solution was poured on top, and the material was kept under a pressure of 2.0 MPa until its total setting. Six molded materials were obtained with this procedure, as shown in Table I.

Characterization

The materials were characterized with IR spectroscopy, thermogravimetry (TG; Shimadzu TGA 50H) in air and nitrogen atmospheres (150 mL/min) at a heating rate of 10°C/min, and differential scanning calorimetry (DSC; Shimadzu 50) under He (50 mL/min) at a heating rate of 20°C/min. The water absorption resistance (ASTM D 570-81) was also evaluated after 24 h, 1 week, and 2 weeks. The Izod impact strength was measured with a 2.75-J pendulum according to ASTM D 256-93 with five test specimens. The fracture

TABLE II
Main Absorptions of Functional Groups Observed for Biopitch, 0% Matrix, and 25% Matrix

Wavenumber (cm ⁻¹)	Biopitch	Matrix (0%)	Matrix (25%)	Assignments
3450	x	x	x	ν of OH and NH
3030–2850	x	x	x	ν of CH
1704	x		x	ν of C=O not conjugated
1735		x	x	ν of C=O of urethane
1670–1450	x	x	x	ν of C=C _{ar}
1230–1200		x	x	δ of C–N
1115	x		x	δ of guaiacyl and siringyl rings
730	x	x	x	δ of C=C cis

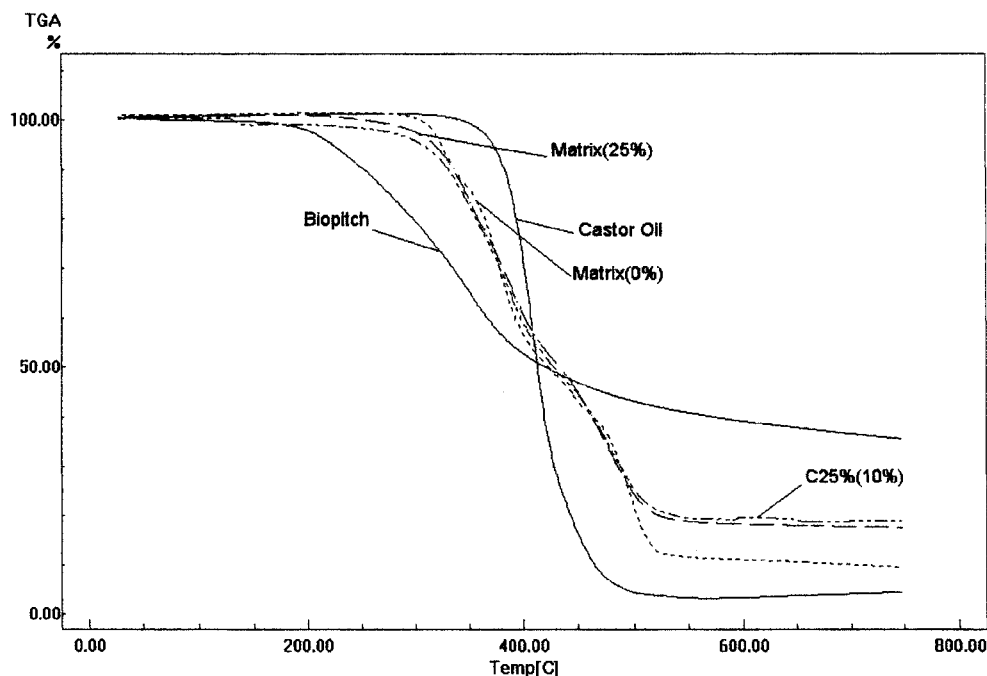


Figure 2 TG curves under an N_2 dynamic atmosphere at $10^\circ\text{C}/\text{min}$.

morphology of the composites was observed with scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Wood tar pitch presented a hydroxyl content equal to 435.7 mg of KOH/g; this made its use as a rigid PU precursor possible.⁴ Castor oil presented a hydroxyl content equal to 164.9 KOH/g.

Figure 1 shows IR absorption spectra for biopitch and PU matrices containing 0 and 25% vegetal pitch as polyols. The PU spectra display an absorption at 1735 cm^{-1} , which is characteristic of the formation of urethane groups. The assignments of the absorption bands are given in Table II.

Figure 2 gives TG curves of polyols (biopitch and castor oil), PUs [Matrix (0%) and Matrix (25%)], and a composite [C25% (10%)] under a nitrogen dynamic

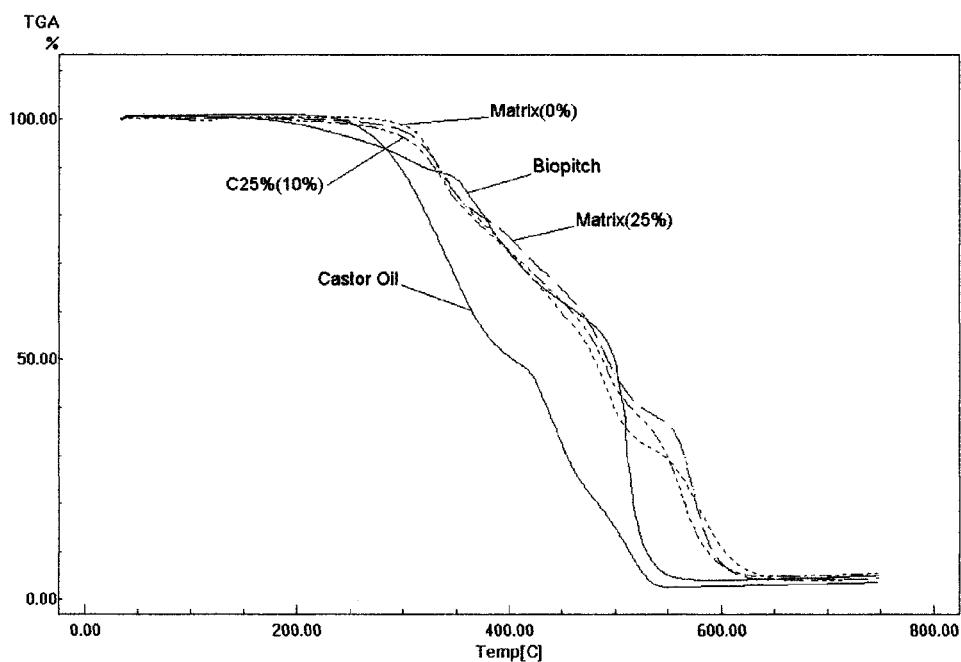


Figure 3 TG curves under an air dynamic atmosphere at $10^\circ\text{C}/\text{min}$.

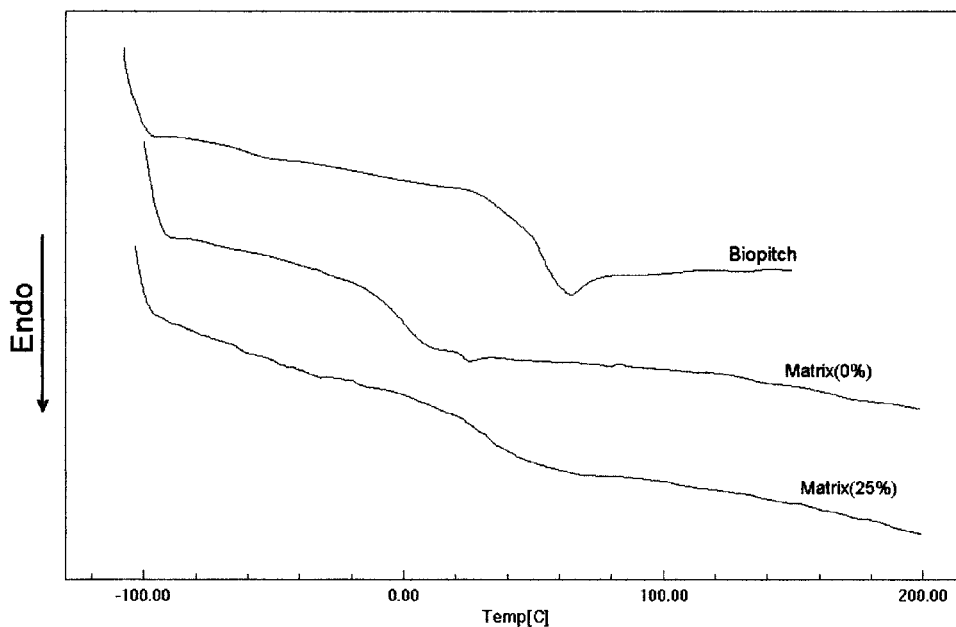


Figure 4 DSC curves (second run) under a helium atmosphere at 20°C/min.

atmosphere. The castor oil degraded in a single step (380–450°C). The biopitch degraded in a continuous event (200–450°C). The thermal stability of the castor oil was superior to that of the biopitch around a 50% mass loss (at 420°C), when the pitch became more thermally stable. This behavior was explained by the high standard of oxygenation of the pitch (22% O), which released endogenous oxygen present in its three-dimensional chain during its pyrolysis and favored self-combustion. This was also due to its con-

siderable aromaticity (50%), which generated 35% of its residual mass up to 750°C. Materials based on these polyols were stable in the range of reagents in isolation. A significant variation was not observed in the thermal behavior of the PUs [Matrix (0%) and Matrix (25%)] and composite [C25% (10%)] with the addition of pitch in the range studied (0–25%).

Figure 3 presents TG curves under an air atmosphere. In a comparison of the *t*-onsets of the polymeric matrices and polyols, an increase in the thermal

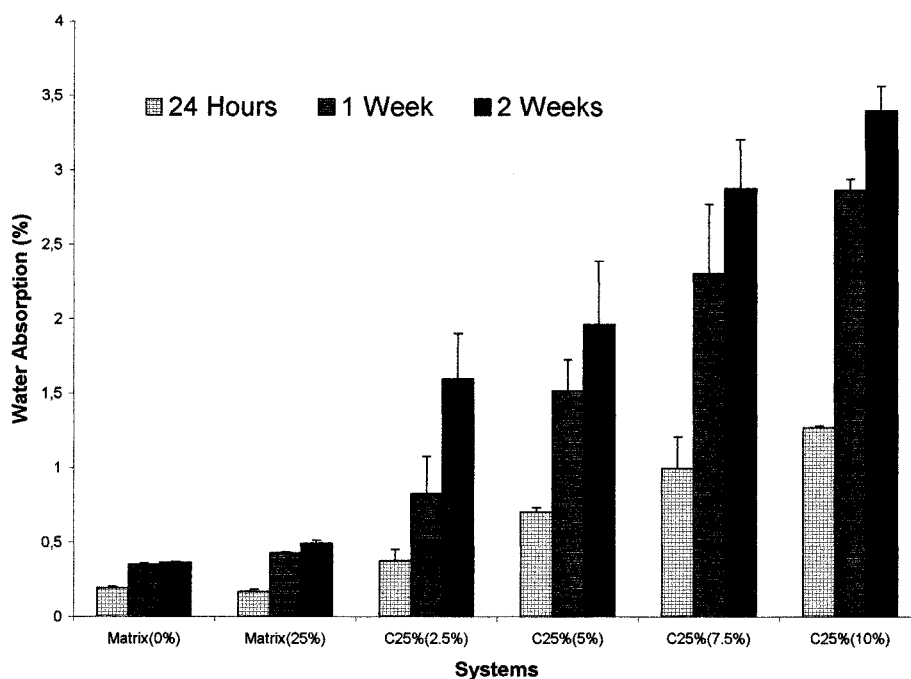


Figure 5 Water absorption at room temperature for the matrices and composites.

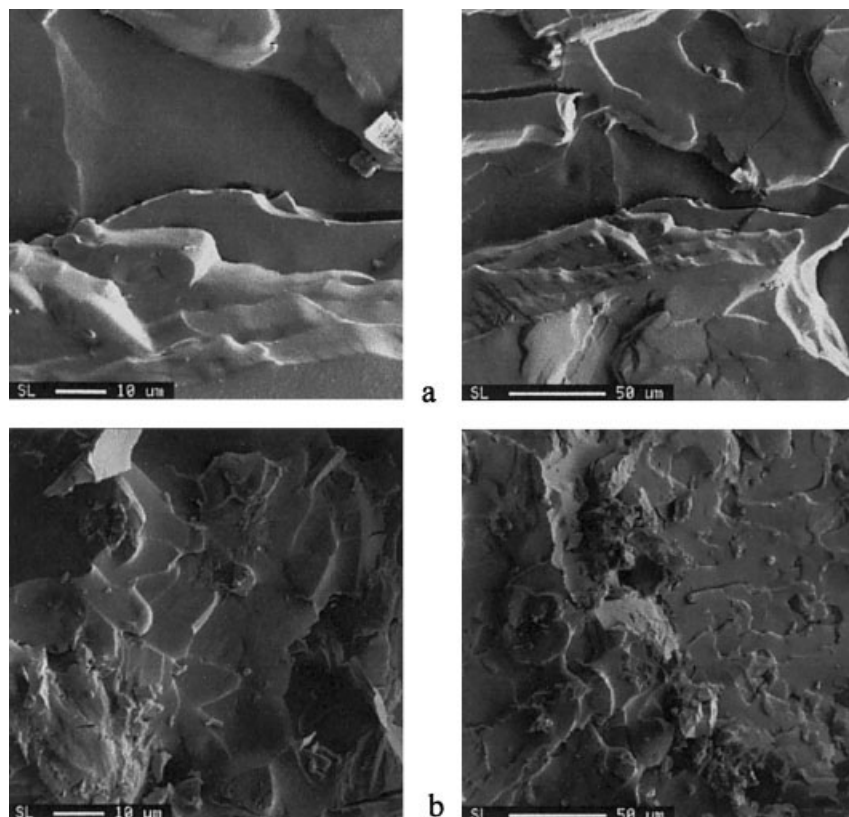


Figure 6 SEM micrographs of (a) PU Matrix (0%) and (b) PU Matrix (25%) with original magnifications of 50 \times (left) and 500 \times (right).

stability for the PU systems can be observed. The biopitch presented greater thermal stability than the castor oil (over a 20% mass loss) because of its rather aromatic three-dimensional arrangement. The thermal stability of the composite containing 10% sisal fibers in relation to the PU matrix did not vary. Similarly to what happens under an N₂ atmosphere, an increase in the thermal stability was not observed with the insertion of pitch in the range studied (0–25%).

DSC curves showed (Fig. 4) glass-transition temperatures (T_g 's) for biopitch at 50°C and for Matrix (0%) at –2°C; they occurred in a rather large temperature range because of the movements of the different chemical groups present in the structure. The addition of biopitch to the structure of PU raised T_g because of the increase in the crosslinking and the resultant decrease in the free volume of the material, as can be observed for Matrix (25%) with $T_g = 33^\circ\text{C}$.

The water absorption resistance results obtained for the materials (Fig. 5) showed their high hydrophobicity. Even when they contained 10% sisal fibers, they absorbed only 3.4% water after 2 weeks of immersion. The matrices absorbed much less than 0.5% water after 2 weeks; this suggests their use in outdoor applications. The incorporation of sisal fibers led to an increase in water absorption because of their hydrophilic character.

Fracture micrographs of PU matrices (Fig. 6) showed only slightly homogeneous materials because the kinetics of the reaction between the polyol and the diisocyanate was too fast and, therefore, generated domains in certain regions. This is characteristic of multiphase polymers.

A morphological study of the composites (Fig. 7) showed a random distribution of the fibers in the matrix, the presence of pores in the structure, and the existence of unreacted biopitch. However, there was adhesion of the sisal fibers to the matrix due to the presence of polymeric materials on the fiber surface

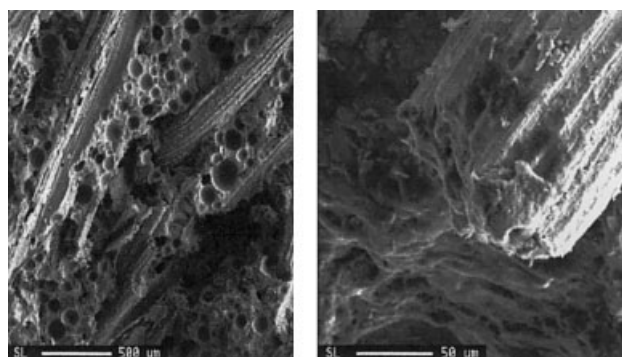


Figure 7 SEM micrographs of C25% (10%) with original magnifications of 50 \times (left) and 500 \times (right).

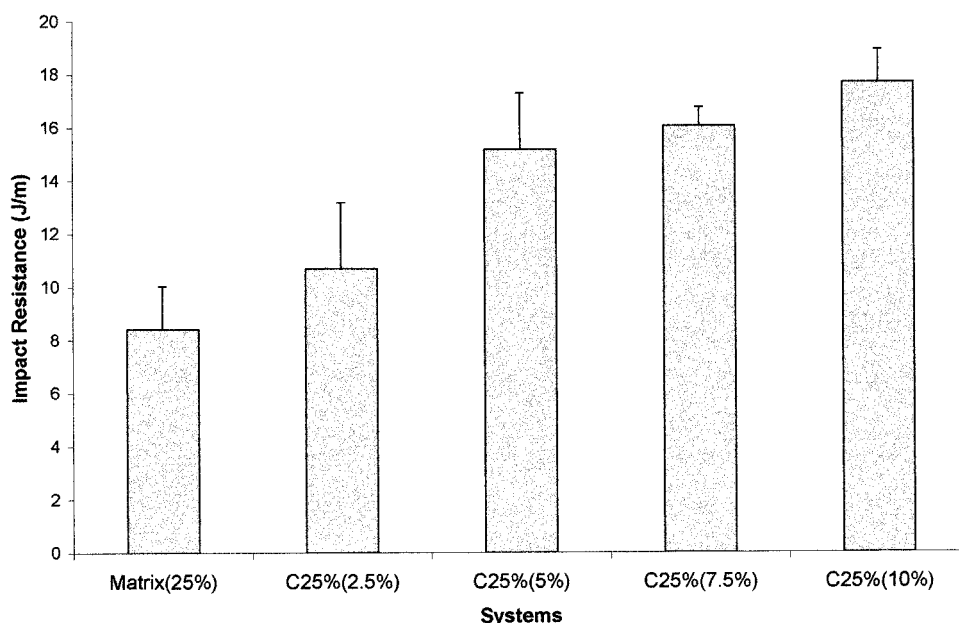


Figure 8 Impact resistance of the composites.

after composite fracture. This certainly reflected positively on its mechanical properties.

The increase in the fiber content in the composites led to an increase in the impact resistance, with values around 17.65 J/m for the composite with 10% sisal fibers (Fig. 8). The PU prepared solely with castor oil, Matrix 0%, was not analyzed in relation to the impact resistance because it was rather flexible, unlike Matrix (25%). This indicated that the inclusion of biopitch increased this propriety significantly by increasing the number of crosslinks and stiffening the polymer.

CONCLUSIONS

Materials with low hydrophilicity and appreciable mechanical resistance were synthesized with a 100% renewable mixture of polyols reinforced with sisal fibers.

Although the biopitch presented significant aromaticity, its inclusion in the 25% polymer did not result in increased thermal stability under N_2 and air atmospheres. However, this polyol increased T_g 's of the matrices and, consequently, the impact resistance. This property rose from 8.42 to 17.65 J/m with an increase in the short sisal fiber content from 0 to 10%. The fibers presented good adhesion to the polymeric matrices, as confirmed by SEM.

The PU matrices presented a low water absorption capacity. The same was observed for the composites, although the sisal fibers were hydrophilic. This suggests their use in outdoor applications.

References

- Gandini, A. *Comprehensive Polym Sci* 1992, Suppl. 1.
- Coelho, J. C. *Biomassa, Biocombustíveis e Biologia*; Ministry of Mines and Energy: Brazil, 1982; p 100.
- Zaicov, G. E.; Artsis, M. I.; Polishcuk, A. Y. *Polym News* 1996, 21, 323.
- Oertel, G. *Polymer Handbook*, 2nd ed.; Hanser: New York, 1994.
- Mello, M. G. *Biomassa Energia dos Trópicos em Minas Gerais*; Labmídia: Belo Horizonte, Brazil, 2001; p 266.
- Prauchner, M. J.; Pasa, V. M. D.; Otani, C.; Otani, S. *Proceedings of Natural Polymers and Composites IV*, Águas de São Pedro, Brazil, 2002; p 62.
- Melo, B. N.; Pasa, V. M. D. *Proceedings of the 5th Congresso Brasileiro de Polímeros*, Águas de Lindóia, Brazil, 1999; p 1802.
- Silvia, A. *Mamona—Potencialidades Agro-Industriais do Nordeste Brasileiro*; Sudene: Recife, Brazil, 1983.
- Oksman, K. *Proceedings of Natural Polymers and Agrofiber Based Composites*, São Paulo, Brazil, 2000; p 203.
- Mano, E. B. *Polímeros como Materiais de Engenharia*; Edgar Blucher: São Paulo, Brazil, 1991.
- Araújo, R. C. S.; Pasa, V. M. D. *J Therm Anal Calorim* 2002, 67, 313.