

Thermal and Morphological Study of Polyurethanes Based on Eucalyptus Tar Pitch and Castor Oil

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ABSTRACT: This article presents the results of the synthesis and characterization of environmentally friendly polyurethanes based on renewable polyols, and specially highlights the use of Eucalyptus tar pitch, a byproduct of the charcoal making industry in Brazil, to obtain PUs. Eucalyptus tar pitch and castor oil PUs synthesized with MDI in THF, catalyzed by dibutyltin dilaurate, were prepared with NCO/OH equal to 1, and vacuum cured. The addition of Eucalyptus tar pitch to the formulation of PUs showed a

tendency to increase the formation of rigid segments, and consequently, to modify thermal stability. SEM micrographs confirm this behavior, displaying different materials. Homogeneous polyurethane elastomers become rigid and acquire lamella structure with the addition of biopitch, as confirmed by tensile strength assays. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3287–3291, 2004

Key words: polyurethanes, morphology, thermal properties

INTRODUCTION

Brazil has an expressive iron-making industry, which uses about 6,000,000 tons of charcoal/year. This industry produces this thermal reducer based on planted Eucalyptus forest, which can be cut in only 7 years in tropical climate. During the slow pyrolysis of Eucalyptus, only about 30% is converted into charcoal; the other 70% is released as volatiles (tar, noncondensable gases, and water). These volatiles can be liquefied to obtain pyrolygneous liquor, which can be reprocessed. The development of applications for Eucalyptus tar is very important to make feasible this model of clean iron making activity. The synthesis of polymers using Eucalyptus tar derivatives seems to be a correct alternative to increase the revenue of the charcoal-making industry, and consequently, to stimulate the use of planted biomass.

Biopitches are fusible solid oligomers obtained from Eucalyptus tar fractionation as a residue of vacuum distillation. They present chemical groups similar to those of lignin (guaiacyl and siringyl units), macromolecular network ($\bar{M}_w = 200\text{--}5000$ g/mol), high hydroxyl content (10–15%), glass transition temperature of about 25–60°C, thermal plasticity, and low aromaticity (50%) in comparison to mineral pitches, and a purely viscous flow.¹ They are constituted basically of carbon (72%), hydrogen (6%), oxygen (22%), and traces of nitrogen.^{1,2} The use of biopitch instead of

lignin in polymer synthesis seems to be more attractive due to its thermoplasticity and its less crosslinked structure, which permits a more effective access to reactive groups.

These biopitches are presently being produced in a distillation pilot plant; however, the Brazilian production potential is about 50,000 tons/year, considering only charcoal from planted forests. Characterization of this product has been made, and the results show a great potential for its use as a precursor of phenolic resins,³ polyurethane,^{4,5} and carbon fibers.⁶

Castor oil, derived from the plant *Ricinus communis*, has its main use in therapeutics such as for gastrointestinal disturbs. The raw oil is constituted basically of 89.5% ricinoleic acid, a triglyceride. From the innovative viewpoint, its chemical structure is of great interest for the oil industry, because it allows a large number of reactions and derivative products.⁷ This oil has been used as a polyol to obtain polyurethanes,⁸ and in this article, it is also used as a kind of biopitch solvent.

The importance of the development of polymeric materials using renewable sources rises from the concern about raw material processing and the development of alternative synthesis routes less hazardous to the environment. Strategically, biomass is without doubt the cornerstone of this technological tendency.

Considering the viewpoint of the polyurethane industry, the use of polyols produced with a closed carbon cycle, without Green House Effect impact, seems to be attractive also, especially if we consider the low cost of these residues.

Several works and patents use basically cellulose and lignin in the synthesis of polyurethanes; however, the use of biopitch as a precursor of polyurethanes along

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TABLE I
Main Events Observed by Polyurethane TG/DTG Curves in Dynamic N₂ Atmosphere and Heating Rate of 10°C/min

Sample/biopitch contents (%)	Event a		Event 1		Event 2		Event 3	
	Weight loss (%)	Maximum degradation (°C)	Weight loss (%)	Maximum degradation (°C)	Weight loss (%)	Maximum degradation (°C)	Weight loss (%)	Maximum degradation (°C)
0%	—	—	14	311	39	369	40	480
25%	—	—	28	346	29	365	27	484
50%	—	—	—	—	35	352	26	462
75%	10	248	—	—	33	345	34	473
100%	14	231	—	—	31	354	15	524

with castor oil is rather promising and innovative. This work has the objective of studying the morphology of polyurethanes based on biopitch and castor oil, and the influence of biopitch on the thermal stabilization of polyurethane to determine the optimal pitch content.

EXPERIMENTAL

The synthesis of polyurethanes first resulted from dosing the hydroxyl content of polyols through acetylation with acetic anhydride and pyridine, countertitred by sodium hydroxide. The materials were synthesized using polymeric 4,4'-diphenylmethane diisocyanide (MDI). Considering the macromolecular and three-dimensional structure of biopitch, and also the structure of polymeric MDI, it is impossible to react and access all hydroxyl groups of biopitch; therefore, the NCO/OH ratio used was equal to 1. The isocyanate excess probably will react with the atmosphere moisture. The reactions were catalyzed with dibutyltin dilaurate in a single step process and cured in vacuum.

Eucalyptus tar pitch was weighed in a 250-mL beaker in varying proportions 0, 25, 50, 75, and 100% of polyol for each formulation. Next, 30 mL THF was added under mechanical stirring to solubilize the polyol. After solubilization, the catalyst was added (1%) and stirred once more. Last, MDI was added and the polymeric solution was kept under stirring for about 10 min. Then, the solution was poured onto a Petri dish and cured under vacuum. After curing, the material was left in a heated oven for 8 h.

The thermal stability of polyurethanes was studied by thermogravimetry (TG) and derivative TG (DTG) in N₂ atmosphere with a heating rate of 10°C/min using a TGAH-Shimadzu apparatus (Table I). The morphology of the materials was studied through their fractures after immersion into liquid nitrogen. Topographies for polyurethanes with 0, 25, 50, and 100% biopitch were analyzed. In this technique, a JEOL JXA 8900RL electronic microscope was used. Samples were previously coated with a gold layer. For tensile strength assays, test samples were used⁹ in

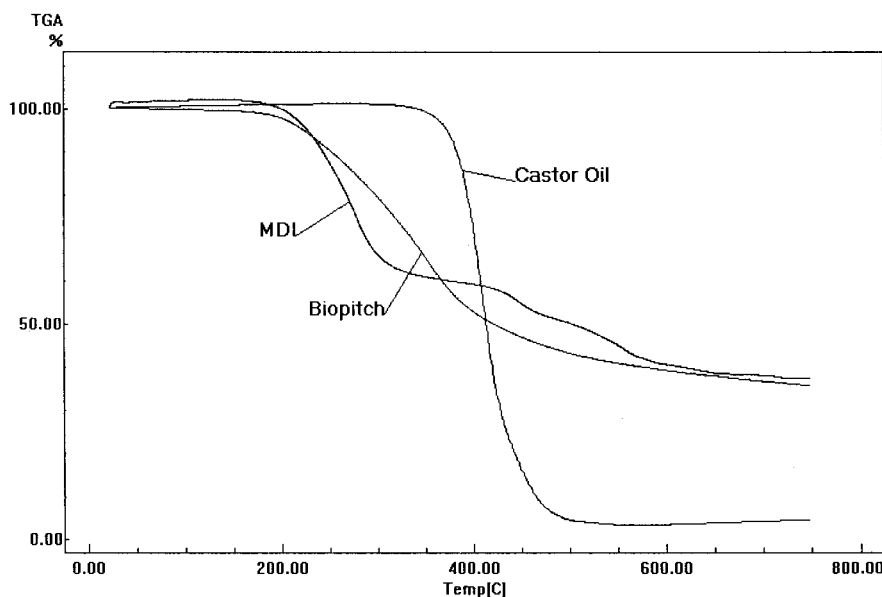


Figure 1 TG curves for Eucalyptus tar pitch, castor oil, and MDI in dynamic N₂ atmosphere.

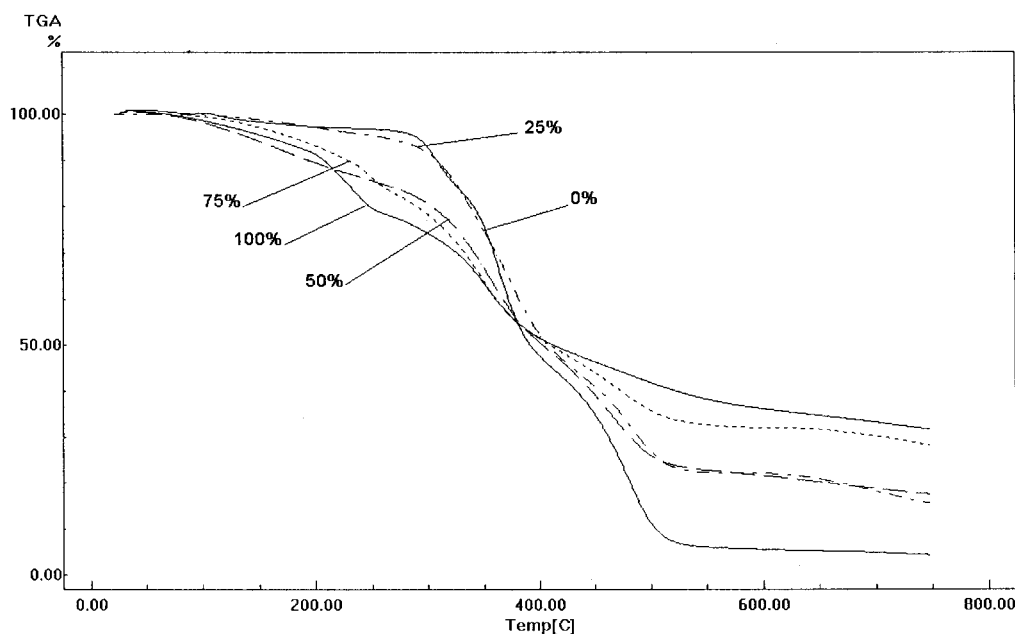


Figure 2 TG curves of polyurethanes in dynamic N_2 atmosphere.

accordance with standard ASTM D638-96 for PUs containing 0% and 25% Eucalyptus tar pitch. For such, a universal assay apparatus, Instron 4200, was used with a cell load of 5 kN, crosshead speed of 50 mm/min, and distance of 10 mm. Average curves were made from five tensile strength assays of each sample.

RESULTS AND DISCUSSION

The functionality of the Eucalyptus tar pitch obtained was 15% hydroxyls or 435.7 mg KOH/g of sample, making viable its use in the generation of rigid polyurethanes. Biopitch showed early to have a highly hydroxylated structure, and not to be able to generate thermoplastic materials,^{10,11} because it favors high crosslinking and the nonlinearity of its oligomeric chains. Castor oil presented functionality equal to 5.5% or 164.9 mg of KOH/g of sample.

TG curves for biopitch, MDI, and castor oil are shown in Figure 1. Onset temperatures (T_{onset}) were as follow: eucalyptus tar pitch, around 210°C; MDI, around 190°C; and castor oil, around 355°C. The lower stability of biopitch in N_2 atmosphere can be understood taking into consideration the high pattern of oxygenation of its oligomeric structure (C = 72%, H = 6%, O = 22%). Oxygen is present mainly as hydroxyl and methoxyl fragments of substituted guaiacyl and siringyl units. In this pyrolysis dynamic, heating biopitch releases endogenous oxygenated fragments, which contributes to the continuous thermal degradation of the material. The initial weight loss observed for biopitch (Fig. 1) occurs due to the distillation of small amounts of volatiles with low

molecular weight. Temperatures higher than about 200°C favor the degradation of biopitch macromolecules, as discussed in the study on Eucalyptus pitch thermal polymerization.² MDI presented thermal deg-

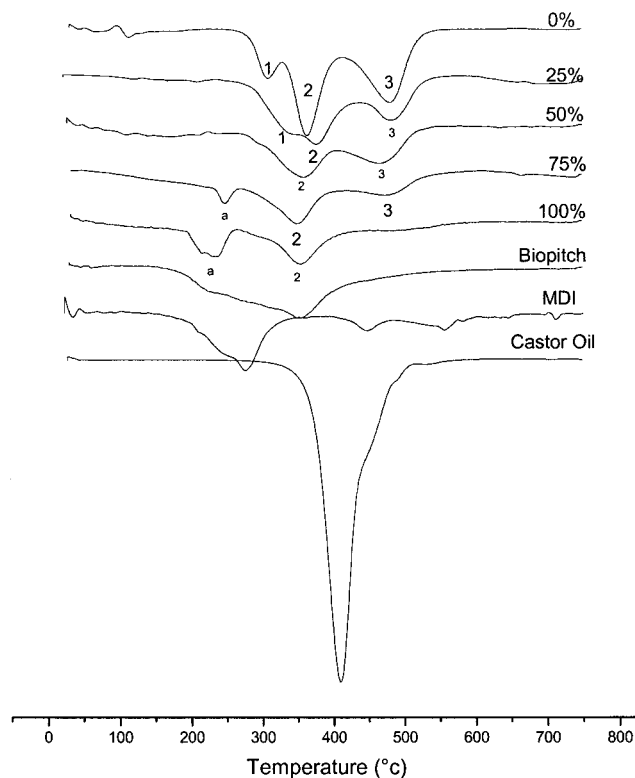


Figure 3 DTG curves of polyurethanes and reagents in dynamic N_2 atmosphere.

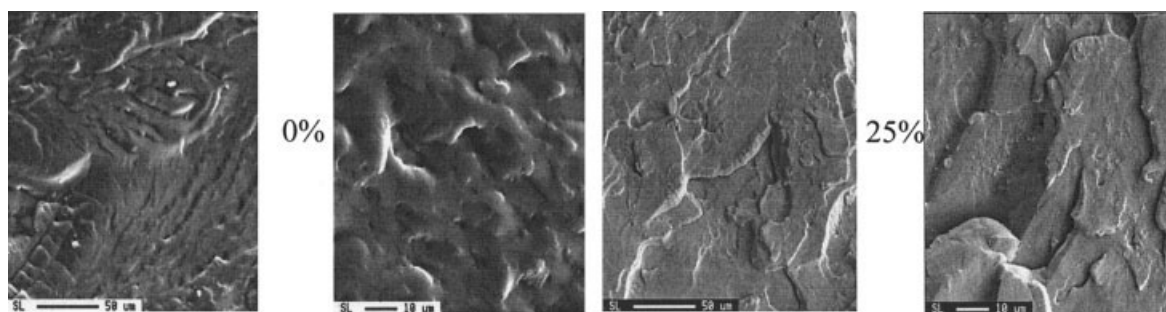


Figure 4 SEM micrographs of PU 0% and 25% Eucalyptus tar pitch enlarged 500 times on the left, and 1300 times on the right.

radiation in three events at about 260, 440, and 550°C. The formation of 35% of carbonaceous residue for both biopitch and MDI, and 3.5% for castor oil, over 500°C could be observed. The high content of carbonaceous residue for biopitch is due to its structure (about 50% of carbons are aromatic as substituted phenolic units). A similar behavior was observed for MDI, which also has an aromatic structure.

PUs in N_2 (Fig. 2), stand out for presenting two well-defined groups of behaviors.^{4,6} Materials with contents of 0 and 25% biopitch present T_{onset} much superior to those with 50, 75, and 100%. This behavior can be explained by the fact that pitch probably presents a maximum content incorporation into the PUs macromolecular structure. From 50% on, biopitch started to segregate in different domains, exhibiting smaller thermal stability due to its high oxygen proportion.

PU (25%) and PU (50%) practically present the same content of carbonaceous residue 14–18%, which should increase with the increase in biopitch content, due to its aromaticity.

PU (25%) presented optimum Eucalyptus tar pitch content, because it has good thermal stability.

DTG curves in N_2 atmosphere (Fig. 3), show the main degradation events for polyurethane samples, biopitch, MDI, and castor oil.

The first DTG curve shows three main degradation events (peak 1, 311°C; peak 2, 369°C; and peak 3, 480°C) for PU0%, based only on castor oil. The first event at 311°C can be related to the degradation of

urethane groups.¹² The second event, at 369°C, is due to the degradation of the castor oil aliphatic structure. The third peak, at 480°C, is due to the degradation of the aromatic structure of polymeric MDI.¹³

Polyurethane samples with 50, 75, and 100% biopitch did not present the first event. For the polyurethane sample with 25% biopitch, this peak almost overlapped the second one. It was observed because the biopitch degradation occurred in a large event. As the biopitch content increased, peak 2 (PU25%, PU50%, PU75% and PU100%) broadened due to urethane groups, castor oil, and mainly biopitch contributions. Polyurethanes with 75 and 100% biopitch presented another peak at 240°C (a) related to the light compounds of biopitch, and mainly unreacted MDI. The reactivity of biopitch is lower than that of castor oil. Therefore, the higher the biopitch content, the higher the unreacted MDI content. For the sample with 100% biopitch, peak (a) was more significant, and the third one almost disappeared, due to the predominance of the contribution of rigid segments (urethane and biopitch) (peak 2).¹⁴

The topographic analysis of these materials is rather relevant because it allows the evaluation of the morphology of the domains created within the material, mainly phase separations and flaw inclusions. Along with other analysis techniques, the topographic images of the polymer can be the starting point to explain a given behavior in relation to thermal stability and the properties related to molecular arrangement, as for

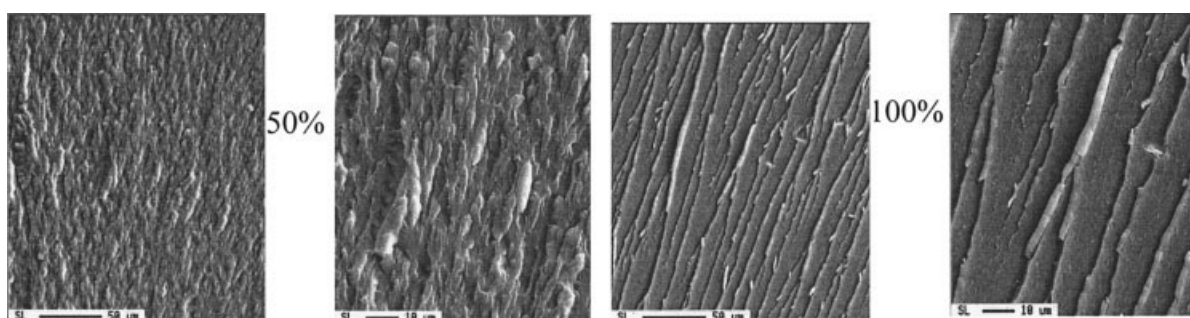


Figure 5 SEM micrographs of PU 50% and 100% Eucalyptus tar pitch enlarged 500 times on the left, and 1300 times on the right.

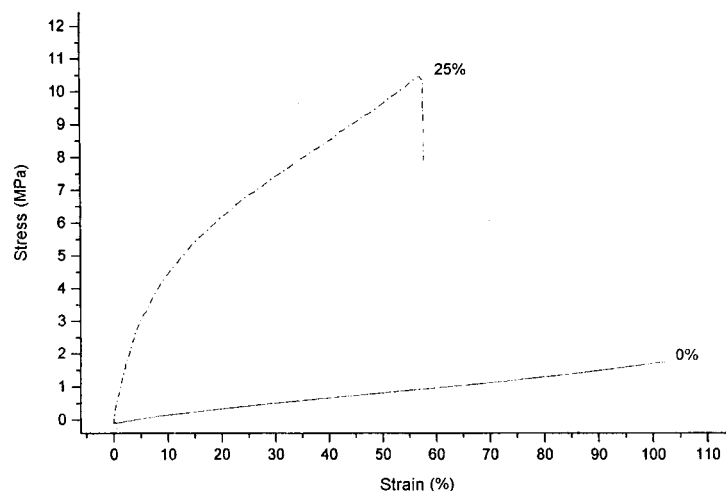


Figure 6 Average strength vs. deformation curves for PUs with 0% and 25% biopitch.

example, swelling due to the absorption of a given solvent by the material.¹⁵

Images of the following materials were obtained: PU(0%), PU(25%), PU(50%), and PU(100%) (Figs. 4 and 5), aiming to evaluate the effect of Eucalyptus tar pitch on PU structure, and on the morphology of the material as a whole.

It was observed that for PU (0%) there is uniformity of fracture with well-defined domains typical of a homogeneous material.¹⁶ Its structure does not present pores, which can be explained by the compaction of the macromolecular chains. This behavior is favored as the biopitch content is increased. The material becomes less segmented, increasing the heterogeneity of the domains, and reaches a lamellar fracture morphology in PU (100%) formed mainly by rigid domains. The images clearly show these observations.

Curves of stress vs. deformation (Fig. 6) show an increase in the elasticity modulus with the increase in pitch content in the molecular structure of polyurethanes. Biopitch participates in the macromolecular structure, increasing the number of crosslinks and making the material more rigid and less segmented. The high biopitch content of the material increases stress at rupture, and also tenacity, the energy necessary for rupture.

PUs 50, 75, and 100% biopitch were not analyzed because it was impossible to prepare test samples due to the high rigidity of the materials.

CONCLUSION

Eucalyptus tar pitch, along with castor oil, is an alternative polyol precursor for polyurethanes. Biopitch, castor oil, and MDI system produced polyurethanes with excellent surface finishing and good compatibility among the reagents. The maximum biopitch content for the elaboration of polyurethanes with good dimensional sta-

bility was 25%. The effects of the addition of Eucalyptus tar pitch on the thermal and mechanical properties could be confirmed by SEM analysis. Biopitch increased the crosslinking and the carbonaceous residue of the PU produced, but decreased its thermal stability (T_{onset}). Eucalyptus tar pitch contributed significantly to the formation of rigid segments due to its three-dimensional and aromatic macromolecular structure, and to the increase in heterogeneity and the reduction of its elastomeric behavior.

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