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THERMAL STUDY OF POLYURETHANE ELASTOMERS BASED ON BIOPITCH–PEG–MDI SYSTEM

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Abstract

Polyurethanes based on biopitch and PEG of distinct molecular masses ($\overline{M}_w$ 1500, 4000 and 6000) were synthesized using polymeric MDI. Different materials were obtained through syntheses using various biopitch content and NCO/OH ratio. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were used to determine their thermal properties. Variations of thermal stability were observed with amorphous and semicrystalline structures depending on the biopitch content and the NCO/OH ratio.

Keywords: biopitch, DSC, PEG, polyurethane, TG

Introduction

Many researchers have considered the use of renewable resources as a potential substitute of petrochemicals. Brazil stands out in the world for its large territorial extension, its tropical climate and its intense production of renewable resources. Some steel industries use charcoal as thermoreducer through homogeneous Eucalyptus forests. Around 67% of all charcoal consumed in Brazil in 1998 was obtained from planted forests [1]. Charcoal carbonization produces gaseous and volatile byproducts, which are recovered forming a complex mixture named wood tar. This recovery produces up to 200 kg of wood tar per ton of charcoal obtained. Wood tar processing consists of its primary distillation to produce oily fractions and biopitch. It is possible to manufacture pharmaceutical, food additives, general chemical, and several polymeric products using these renewable raw materials [2, 3].

Elemental analysis of biopitch from wood tar with O/C and H/C ratio 0.25 and 1.07, respectively, has shown its aromatic nature and high oxygen content (24%) [4]. The structure of wood tar biopitch has revealed it to be different in comparison to coal tar pitch (with O/C and H/C ratio 0.6 and $6.0\cdot10^{-3}$) or petroleum pitch (with O/C and H/C ratio 0.8 and $4.0\cdot10^{-3}$) [5]. Biopitch is similar to lignin, and has guaiacyl and siringyl units and their derivatives in its structure. However, lignin is a macromolecular network while biopitch shows the same chemical groups, despite having

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smaller molecular mass and a distinct thermoplastic behavior [2, 4]. Polymers based on biomass like phenolic resins, polyurethane foams and elastomers were produced through synthesis taking advantage of the chemical similarity between lignin and biopitch [6, 7].

Experimental

Materials

Wood tar was obtained by condensing smoke given off by Eucalyptus charcoal production masonry kilns. The fractionating of tar generates biopitch by vacuum distillation as a solid residue in a pilot plant (temperature=200°C, pressure=30 mm Hg, 50% mass/mass).

Poly(ethylene glycol) (PEG) of various molecular masses ($\overline{M}_w$ 1500, 4000 and 6000) and Polymeric MDI-4,4'-diphenylmethane diisocyanate were used in the synthesis of polyurethanes (PUs). Polyurethanes were obtained from a mixture of biopitch and PEG in one shot with MDI using tetrahydrofuran (THF) as a solvent and dibutyltin dilaurate (DBTDL) as catalyst. Samples were synthesized with different biopitch content (0, 10, 20, 30, 40 and 100%) and molar NCO/OH ratios (1.0, 1.5 and 2.0), producing 51 samples altogether.

Measurements

Thermogravimetric analyses (TG) measurements were carried out using a Shimadzu TGA-50 under dynamical nitrogen and air atmosphere with a flow rate of 150 mL min^{-1} and a heating rate of 10°C min^{-1} in the range of 25 to 750°C. All samples had approximately 6 mg.

Differential scanning calorimetry (DSC) analyses were carried out using a Shimadzu DSC-50. The samples were first scanned up to 150°C; thereafter cooled and recorded a second time up to 200°C. T_g was determined from the second run. Measurements were carried out under a helium atmosphere with a flow rate of 50 mL min^{-1} and a heating rate of 20°C min^{-1}. All samples had approximately 15 mg.

Results and discussion

Figure 1 shows TG curves for biopitch in different atmospheres of air and nitrogen. Thermal stability of biopitch in both atmospheres shows the same degradation behavior up to nearly 200°C. Over this temperature, biopitch showed high stability in air atmosphere. In literature, lignin presented higher thermal stability in air than in nitrogen atmosphere, which is attributed to condensation reactions that occurred between air oxygen and the oxygen in the lignin [8]. The similarity between the chemical groups of biopitch and lignin leads us to attribute this behavior to the same cause.

The DSC curve for biopitch (second scan) is shown in Fig. 2. The well-defined glass transition temperature was observed at 28ºC means that biopitch can be consid-

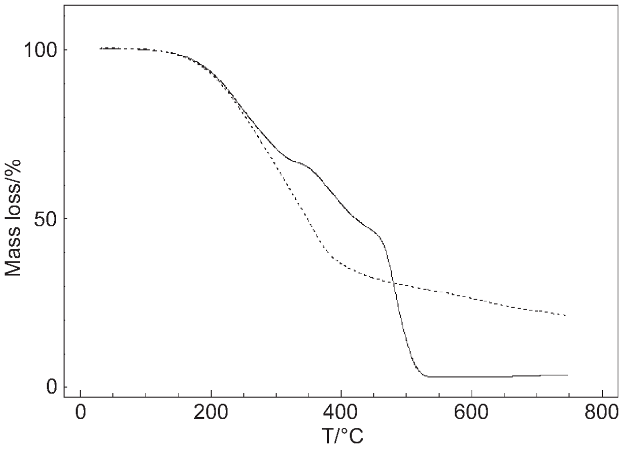

Fig. 1 TG curves for biopitch in dynamical air (——) and nitrogen (- - -) atmospheres at 10°C min^{-1}

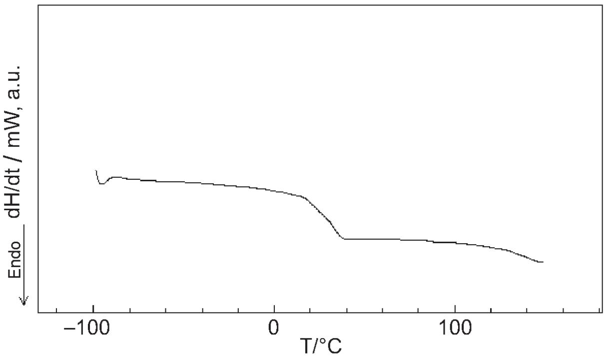

Fig. 2 DSC curve (second scan) for biopitch in dynamical helium atmosphere at 20°C min^{-1}

ered an amorphous material. A previous study reported that the isolated lignin was amorphous and thermosetting materials with glass to rubber transitions (T_g) between 90 to 180°C [9]. Biopitch T_g is inferior (25 to 50°C) due to its lower molecular mass presenting a thermoplastic behavior.

Figure 3 shows the effect of biopitch content in thermal stability of polyurethanes (air atmosphere). The use of biopitch as polyol reduces T_{onset} of PUs due to its high oxygen content. Therefore, biopitch inhibits polymeric degradation in air above 400–450°C. A similar behavior is observed in Fig. 1 for TG curves of biopitch.

Figure 4 shows the TG curves for PUs with 20% of biopitch content, with different PEG molecular masses ($\overline{M}_w$ 1500, 4000 and 6000). These curves show a similar thermal stability for PUs based on PEG 4000 and 6000, higher than for PU based on PEG 1500. The derived thermogravimetric curves (DTG) show two events for elastomer degradation relative to the segmental nature of polyurethanes. It was observed in

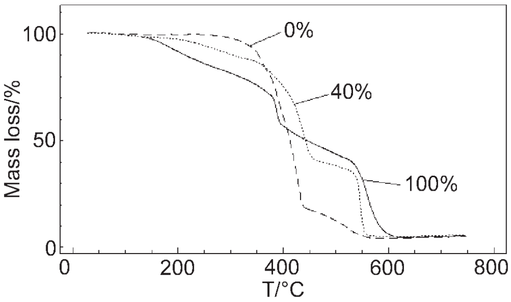

Fig. 3 TG curves for PUs based on PEG 4000 with different biopitch content (NCO/OH=2.0) in air atmosphere

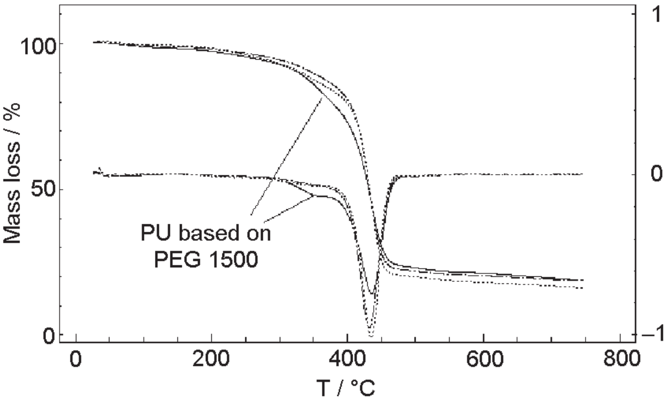

Fig. 4 TG and DTG curves for elastomers based on biopitch (20%) and different molecular masses of PEG (1500, 4000 and 6000) with NCO/OH ratio of 1.5 (nitrogen atmosphere)

polyurethane studies that urethane bonds present lower stability than structures with soft segments (polyols) [10]. TG curve for PU based on PEG 1500 presents lower thermal stability. This fact can be observed on DTG curves, which showed the first event better defined for samples based on PEG 1500, since short chains have higher hard segment content. On the other hand, DTG curves for PUs based on PEG 4000 and 6000 barely showed the same event.

TG curves for polyurethanes based on PEG 4000 with different biopitch content (0, 10, 40 and 100%) in nitrogen atmosphere in Fig. 5 show that the thermal stability changes with biopitch content, and present the same behavior for all set of polyurethanes with PEGs ($\overline{M}_w$ 1500, 4000 and 6000). In nitrogen atmosphere, whenever the biopitch content increases, a decrease in degradation temperature of polyurethanes occurs, as a consequence.

The DSC curves for PUs with different biopitch content, NCO/OH ratios and molecular masses of PEG are shown in Figs 6, 7 and 8, respectively. Figure 6 shows DSC curves with different biopitch content for PUs based on PEG 4000 and

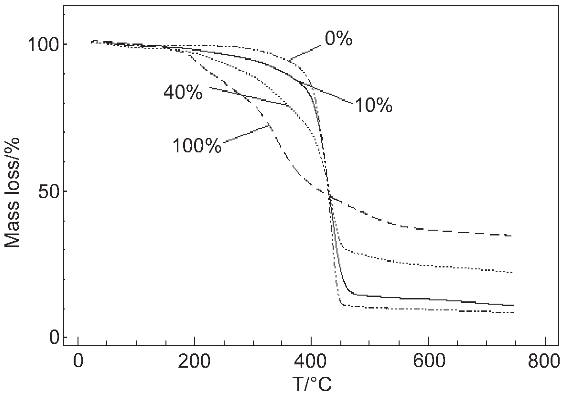

Fig. 5 TG curves for elastomers based on PEG 4000 and different biopitch content (NCO/OH=1.5) in nitrogen atmosphere

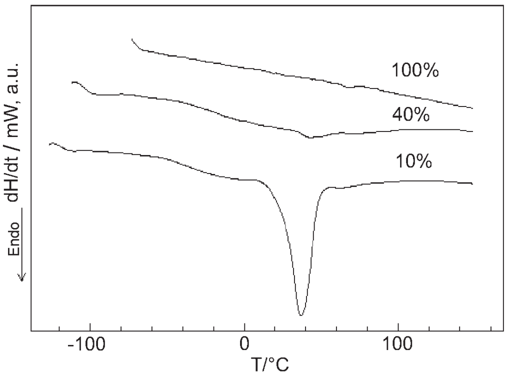

Fig. 6 DSC curves for PUs based on PEG $\overline{M}_w$=4000, NCO/OH=2.0 varying biopitch content (10, 40 and 100%)

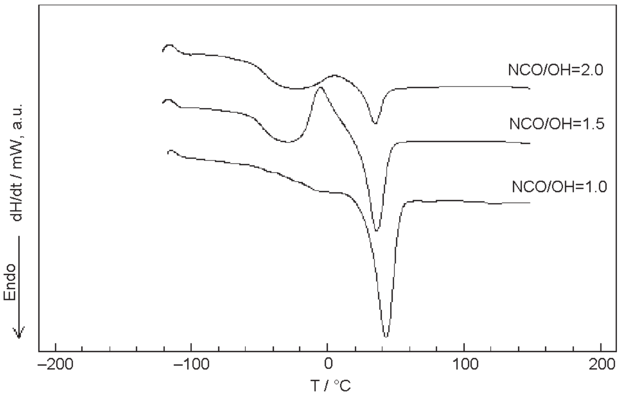

Fig. 7 DSC curves for PUs based on PEG 6000 and biopitch content of 20% varying NCO/OH ratio

NCO/OH ratio 2.0. It can be observed that polyurethane with lower biopitch content (10%) showed lower T_g (–44°C) and endotherm (37°C), which indicates the presence of some crystallinity in this sample. Addition of biopitch to PUs shifts T_g to higher values up to 40% of biopitch content (T_g=–18°C). With increasing biopitch content, T_g becomes more defined and broader, which may be assigned to a reduction of crystallinity. It was not possible to determine T_g or any transition in materials based only on biopitch (100%). An increase in crystallinity with increasing soft segments was observed in DSC curves for samples based on PEGs with different molecular masses (Figs 7 and 8). While all samples based on PEG 1500 were amorphous, those samples based on PEG 4000 and 6000 presented crystalline transition and melting endotherm for low biopitch content and NCO/OH ratio. NCO/OH ratio had a great influence on these polyurethane structures. A decrease in crystallinity was observed

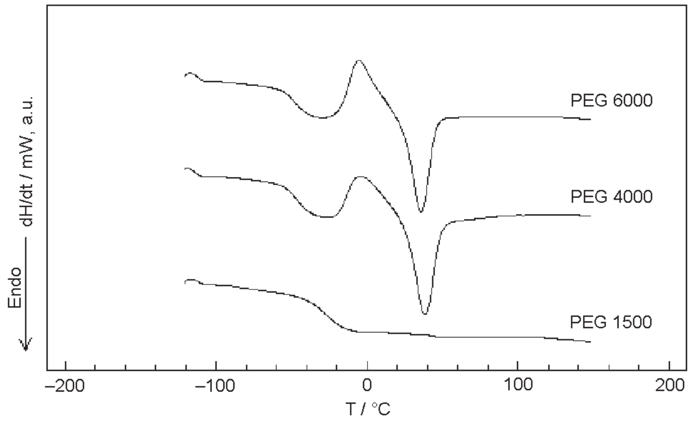

Fig. 8 DSC curves for PUs based on PEG of molecular masses 1500, 4000 and 6000, NCO/OH ratio=1.5 and 20% biopitch content

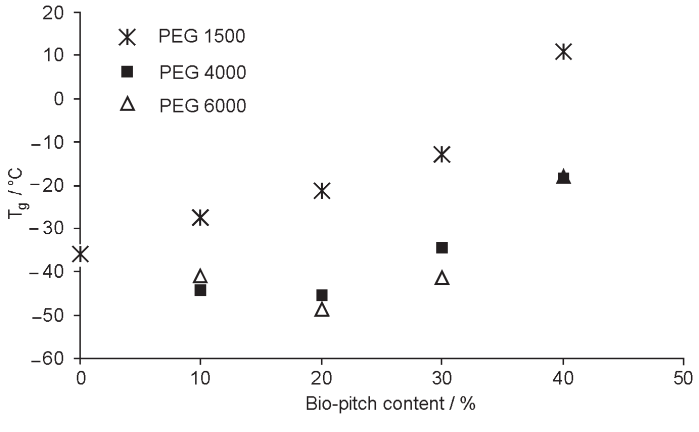

Fig. 9 Effect of biopitch content on T_g values of polyurethanes based on PEG 1500, PEG 4000 and PEG 6000

with increasing NCO/OH ratio (Fig. 7). T_g is the most clearly defined and increases with higher NCO/OH ratio.

Figure 9 shows that polyurethanes based on PEG with lower molecular mass presented higher T_g values. PUs based on PEG and biopitch showed a slight increase, while the literature reports a proportional increase in lignin content for polyurethanes based on Kraft lignin and PEG [9].

Conclusions

- It was possible to obtain different polyurethane elastomers based on biopitch and PEG, varying parameters as PEG molecular masses, NCO/OH ratio and biopitch content.
- The Eucalyptus tar biopitch studied showed different degradation behaviors in air and nitrogen atmospheres, similar to lignin as described in the literature. After a mass loss of 20%, biopitch showed greater stability in air atmosphere. About 50% of the biopitch mass is lost at 480°C. Biopitch has a defined T_g at 28°C.
- Thermogravimetric analysis results of polyurethanes (nitrogen atmosphere) presented a decrease in thermal stability with addition of biopitch, regardless of the molecular mass of PEG and the NCO/OH ratio used. PUs with higher concentration of hard segments has lower stability. TG curves of polyurethanes (air atmosphere) showed that addition of biopitch on PUs retards thermal degradation above 400°C. This behavior can be important in the development of applications in which safety is an essential aspect.
- Polyurethanes with higher biopitch content, higher NCO/OH ratio, and lower molecular mass of PEG presented crystallinity in a smaller extension due to the inferior concentration of soft segments, and therefore, a higher T_g.

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