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Vegetable Oil Based-Polymers Reinforced with Wood Flour

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Liquid polymer precursors were synthesized from vegetable oils to be utilized in the preparation of oil based-resins to be later reinforced with a filler also obtained from natural sources. In this work, an unsaturated oil, tung oil, produced in the region was selected as raw material. The vegetable oil was chemically functionalized to obtain a polyol to be further used in polyurethane formulations. Different analysis techniques were used to investigate the hydroxyl content in the modified oil. Oil based composites containing pine wood flour as filler were prepared and mechanically tested.

Keywords: natural polyol; reinforced polyurethanes; vegetable oil; wood flour

INTRODUCTION

As the environmental considerations become more severe around the world, there is an increasing demand for raw materials based on renewable resources for the production of eco-friendly final materials. Due to its versatility, polyurethanes have been frequently selected for different applications. During the last years, there has been an increasing interest in replacing the commonly used polyols derived

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from the petroleum industry by natural oil based polyols in the formulation of polyurethanes. Vegetable oils are abundant and widely available; they are relatively low cost materials, which offer potential biodegradability.

The oils of interest for the purpose of polyurethane (PU) production consist of triglyceride molecules, containing unsaturated fatty acid chains. These triglycerides have various reactive sites, which are able to be reacted/modified in order to obtain a product of interest for the polymer industry [1]. Natural polyols can be obtained by chemical modification of the vegetable oils introducing hydroxyl groups in the unsaturated triglyceride by hydroxylation of carbon-carbon double bonds and/or by alcoholysis of the triglyceride with triethanolamine to obtain mainly a monoglyceride (Fig. 1) [1,2].

Tung oil is obtained from the seeds of the tung tree [3] and the main constituent of the triglyceride molecules is the elaeostearic acid that contains 3 conjugated unsaturations [4]. This characteristic makes it an excellent product to be used in the paint and varnish industry as drying oil due to its fast polymerization in presence of oxygen [5]. These multiple carbon-carbon double bonds are also capable to be reacted to introduce hydroxyl groups through a hydroxylation reaction.

On the other hand, the use of wood flour is an interesting alternative for the production of reinforced polyurethanes, thus increasing the utilization of low cost raw materials from widely available natural sources.

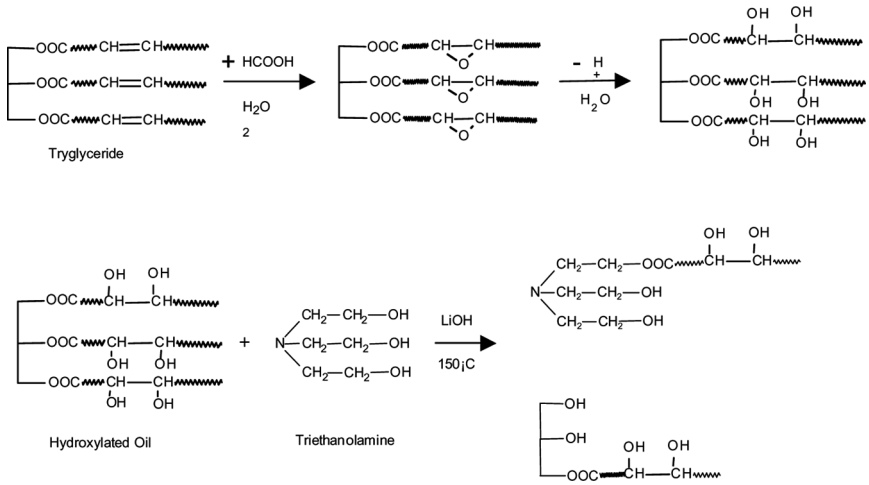


FIGURE 1 Simplified schematic steps of the modification of the unsaturated vegetable oils to polyols.

The focus of this work has been the synthesis and characterization of a polyol based on a tung oil and its utilization in the preparation of wood flour reinforced polyurethanes. The effect of the filler incorporation on the thermal and mechanical properties of the composites was also investigated.

EXPERIMENTAL

Materials

The natural polyol was obtained from tung oil (Cooperativa Agrícola Limitada de Picada Libertad, Argentina, saponification value = 223 mg mg KOH/g, acid number = 2.11 mg KOH/g) and castor oil (Parafarm®, Argentina, hydroxyl value = 169.3 mg KOH/g).

Hydrogen peroxide (30 wt.) and formic acid (88 wt.) from Laboratorios Cicarelli were used in the hydroxylation reaction of the tung oil.

The hydroxylated tung oil was functionalized by alcoholysis with triethanolamine (>99%) from Laboratorios Cicarelli. Lithium hydroxide (>99%) from Fluka was used as catalyst in this reaction.

In the preparation of the polyurethanes, a 4,4′-diphenylmethane diisocyanate (MDI) prepolymer (Rubinate 5005, Huntsman Polyurethanes, USA) with an equivalent weight of 131 g/eq was utilized.

Pine wood flour (Jorge Do Santos Freire, Buenos Aires, Argentina) was selected as the reinforcement/reactive filler. The wood flour average particle size was $\leq$64 μm (by sieving).

Wood flour and polyol were dried before use, in a vacuum oven at 70°C until reaching constant weight.

The hydroxyl value of the wood flour was determined using a back titration technique. A measured weight of wood flour was mixed with excess of MDI. After the reaction was completed, the free NCO groups were determined according to a technique described elsewhere [6]. The resulting value was 233.3 mg KOH/g.

Synthesis of Tung Oil-Based Polyols

Hydroxylated Tung Oil (HTO)

Hydrogen peroxide solution and formic acid were added and stirred in a reactor at 40°C. Tung oil was added drop wise while the temperature was kept between 40 and 50°C during 3 h. After that, the final product was cooled down to room temperature and it phase-separated in two layers. The upper layer was distilled under vacuum to eliminate the remaining water and acid. The simplified schematic of the reaction was shown in Figure 1.

Alcoholysed Hydroxylated Tung Oil (AHTO)

The hydroxylated tung oil, dry triethanolamine, and lithium hydroxide (catalyst) were added together in a reactor and mechanically stirred. The temperature was raised to 150°C in 0.5 h and it was kept at this value for 2.5 h. The catalyst was added as 0.2 wt%. of the total reactants (Fig. 1).

Polyurethane Preparation

The AHTO was used for the preparation of neat polyurethane and wood flour – composites. The index (equivalents NCO/equivalents OH) was adjusted to 1.10. The modified polyol (previously dried) was dissolved in tetrahydrofuran (THF) in order to decrease its viscosity and to slow the reaction to allow for good mixing. After the MDI (or MDI plus filler, in reinforced polyurethanes) was added, the system was mechanically mixed for 20 seconds. Then the reactive mixture was cast to a metal mold of 14 cm of internal diameter. The THF was allowed to evaporate in the open mold, then the mold was closed and the sample cured at 75°C under a pressure of 4 MPa. As a result, 1 mm-thick plates were obtained. Composites with different WF contents were molded according this procedure.

Physical and Chemical Characterization of the Oil-Based Polyol

The concentration of hydroxyl groups in the raw tung oil and derived polyol was measured as hydroxyl number [6]. The viscosity of the two materials at room temperature was determined with a Brookfield viscosimeter.

Size exclusion chromatography (SEC) was used to characterize the distribution of reaction products during the different steps of the polyol synthesis. The carrier was tetrahydrofurane (THF) at 1 cm^3/min and the apparatus was a SEC, Knauer K-501 (RI detector Knauer K-2301 equipped with a set of Phenomenex Phenogel 5 μ-columns: 50 A, 100 A, and M2).

Characterization of the Polyurethanes

Microscopy

Scanning Electron Microscopy (SEM) was used to obtain micrographs of the fracture surfaces of the composites tested in tensile mode (scanning electron microscope Philips model SEM 505). Microscopy specimens were coated with gold before the analysis.

Tensile Tests

The mechanical properties of the neat polyurethane formulated with tung oil based polyol were analyzed by tensile tests. Specimens of each sample were cut from the plates and tested at room temperature and 1 mm/min in an INSTRON 8501 Universal testing machine, according to the ASTM D638-94. At least four specimens of each sample were used, and the average values are reported.

Impact Tests

Fracture Puncture tests were carried out using a falling weight impact tower (Fractovis, Ceast). Samples with diameters of 14 cm, clamped on a supporting ring of 75 mm diameter, were impacted with a hemispherical tipped dart at an incident speed of 2 m/s, using an impactor mass of 18.9 kg. At least 5 specimens for each material were impacted.

The impact resistance (associated to crack initiation) was calculated according to accepted techniques for plastics and composites [7].

RESULTS AND DISCUSSION

Tung Oil-Based Polyol

The hydroxyl and viscosity values of the unmodified oils and the derived polyols were measured and compared. Due to the modification, the hydroxyl value increased significantly from essentially zero in the tung oil to 434 mg KOH/g in the final polyol, an acceptable value for its use in polyurethane formulations. On the other hand, the viscosity also increased with the modification (from 160 cp in the oil to 98700 cp in the polyol) as a result of the intermolecular hydrogen bond interactions present in the polyols.

Additionally, as a consequence of the chemical modification of the tung oil, the resulting polyol presents not only a change in molecular weight, but also a broadening of the molecular weight distribution, as measured with polystyrene standards.

The size exclusion chromatogram (not shown) of tung oil presents essentially one peak that corresponds to the triglyceride. However, after modification, the broadening of the chromatogram at lower retention volumes indicates the formation of higher molecular weight species. This result corresponds to possible polymerization or aggregation of the highly hydroxylated molecules and it is also affected by an aberration problem previously observed by John *et al*. [8]. He reported this effect in the molecular weight of triglycerides when polystyrene was used as standard.

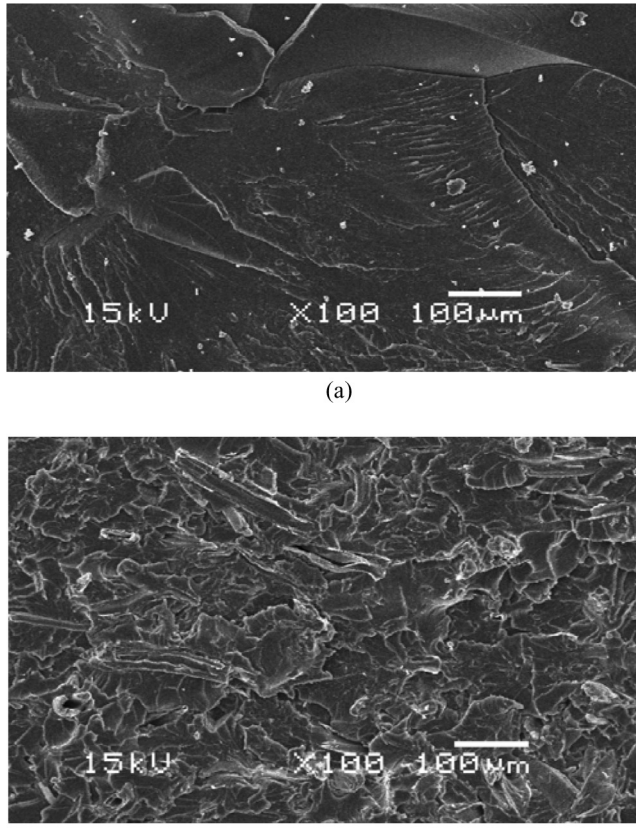
Because of the second step in the modification reaction (Fig. 1), the final polyol also contains species of lower molecular weight than the original triglyceride, which appear at higher elution volumes.

POLYURETHANES

Morphological Analysis

Composite Polyurethanes from Tung Oil

Figure 2 shows the fracture surface of rigid polyurethanes formulated with the tung oil-based polyol (AHTO) without reinforcement (Fig. 2a) and with 10 wt. of wood flour (Fig. 2b). The unfilled polymer



(a)

(b)

FIGURE 2 Fracture surfaces of tung oil based polyurethane (a) and 10 wt.% wood flour filled composite (b).

TABLE 1 Mechanical Properties of the Tung Oil-Based Polyurethane and Wood Flour Composites

	Tensile modulus (GPa)	Tensile strength (MPa)	Impact resistance (MPa)
0% WF	0.91 ± 0.12	26.00 ± 2.56	164.9 ± 25.0
10% WF	1.23 ± 0.13	35.65 ± 1.75	229.0 ± 21.9
30% WF	3.03 ± 0.40	44.90 ± 3.06	279.3 ± 36.2

shows an essentially fragile fracture surface. The surface of the composite is substantially more irregular than that of the neat polyurethane. Additionally, the wood flour (WF) is well dispersed into the polyurethane matrix and there is good adhesion between fiber and matrix, as it was expected from the polar nature of both components.

Mechanical Properties

Polyurethane Composites

The tensile properties were evaluated as a function of the WF content and the results are presented in Table 1. The addition of WF to the polyurethanes results in the increase of the tensile modulus and also the strength of the material. In both cases the improvement is significant and the wood flour acts as a real reinforcement.

Additionally, it is quite interesting to notice the improved impact properties of the composites with respect to the unfilled polymer, a 69% increase of the impact resistance was observed in the 30 wt.% wood flour composite.

All the mechanical properties measured indicated a very good dispersion of the wood flour and strong interfacial adhesion with the matrix, such as it was shown to occur in the microscopic observation of the fracture surfaces of the composites.

CONCLUSIONS

A tung oil-based polyol was prepared to achieve a high hydroxyl concentration, useful to be used as reactant in the production of rigid PU. The resulting tung oil based polyol required the addition of a solvent to decrease the high viscosity prior to be used as a reactive in polyurethane formulations.

Wood flour was used as reinforcement of the resulting polyurethanes and composites were prepared in the range of 0–30 wt% wood flour. The chemical nature of the reinforcement and the matrix selected contributed to a very good dispersion of the wood flour, as well

as good interfacial adhesion. These characteristics were analyzed from microscopic observations and further mechanical characterization of the materials.

The wood flour is acting as a true reinforcement for this polyurethane system, as shown by the increased modulus and strength with addition of WF. Additionally, the impact properties of the material are much improved by addition of the wood flour reinforcement.

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