



## Liquefied agricultural residues for film elaboration



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### ABSTRACT

Agricultural residues (corn stover, corncob, vine shoots and blueberry tree pruning) with low added value were converted through liquefaction into liquefied products. Their capability to form films was evaluated. Results indicated that liquefied products production under liquefaction conditions is completely feasible with yields in the case of corn residues above 90%. The  $I_{OH}$  and viscosities were in the range of 309–441 mg of KOH/g and 0.16–0.19 Pa · s, respectively. These values make the liquefied agricultural residues an interesting alternative to be considered as constituent in liquefied-based materials and composites elaboration. On the other hand, homogeneous, opaque and dark brown flexible films, using weight ratio of (liquefied agricultural residue/starch)/glycerol of (90/10)/30, were produced. The films obtained with corn residues as starting material showed adequate behavior considering physical and mechanical features. DMA measurements for liquefied corncob-films showed higher values of thermal and dynamic mechanical parameters ( $T_g$ : 112 °C;  $E'$ : 42 MPa until 110 °C) compared to control film (starch/glycerol: 70/30), which showed a material with higher thermal stability. The results demonstrated the suitability in the conversion of different renewable and abundant resources into liquid form and their physico-chemical properties for first step film production, which might have interesting perspectives in polymer processing area for bioplastics development in agricultural applications.

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### 1. Introduction

Lignocellulosic residues are an abundant, inexpensive and available source of raw material which shows good perspectives as feedstock for polymer and biomaterial production (Gerssen-Gondelach et al., 2014). In this context, among the numerous novel potential products researched under a green chemistry concept, precursors and additives from natural polymeric substrates have attracted considerable attention (Belgacem and Gandini, 2008; Gandini, 2011). One possible way to obtain these high added value polymeric products is the liquefaction of lignocellulosic biomass. In that sense, liquefaction of lignocellulosic residues from agricultural and industrial activities, which are mainly discarded, used as animal feed or for energy requirements, is a promising alternative to obtain highly reactive viscous liquid with suitable physical and chemical features used commonly as precursor or additive for polymer synthesis, especially polyurethane products. In general, liquefaction of lignocellulosic materials comprises a complex set of reactions taking place on the polymeric components of the

material, such as esterification or etherification of free hydroxyl groups in cellulose or lignin as well as reactions that cause degradation of the biomass constituents (Shiraishi et al., 1985). Liquefied products derived from liquefaction of lignocellulosic biomass using glycols have a large number of oxygen-containing reactive functional groups that are fragments of cellulose, hemicelluloses and lignin constituents (Wang et al., 2008; Briones et al., 2013).

Liquefied products obtained from liquefaction of lignocellulosic biomass by glycols as solvent has been studied intensively by several authors (Kurimoto et al., 1999; Yamada and Ono, 2001) to obtain polymer products e.g., polyurethane foams (Yao et al., 1995), epoxy resins (Kobayashi et al., 2000) and polyurethane adhesives (Juhaida et al., 2010) which are widely used in many fields as structural, cushion, insulation, electrical, flotation and packaging materials.

In recent years, scientific interest in applying liquefaction to other kinds of bioresources has grown. Following this trend, during last decade, several agricultural residues have been successfully modified using glycols for obtaining bio-based polyols and/or polyurethane products (Liang et al., 2006; Wang and Chen, 2007; Hassan and Shukry, 2008; Yan et al., 2008, 2010; Chen and Lu, 2009; Gao et al., 2010; Briones et al., 2012; Hu et al., 2012; Hu and Li, 2014a,b).

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In order to search novel applications of liquefied biomass, a very attractive possibility might be the use of liquefied products as filler or polymer matrix in the production of thermoplastic composites for packaging applications. Doh et al. (2005) demonstrated that the addition of liquefied wood as filler increase of stiffness and tensibility of the composites showing significant effects on. Recently, self-crosslinking and film formation ability of liquefied products from black poplar wood was preliminary studied by FT-IR and measurements of the drying stages (Budija et al., 2009), which could open new application fields in more effective usage of liquefied biomass. In this context, much remains to be done in respect of this matter.

On the other hand, the liquefied product obtained by liquefaction using glycols as solvent could also help to improve the processability during the film preparation, taking into account that glycerol, a common plasticizer in thermoplastic material synthesis, is used as reaction solvent. It is known that plasticizers with features such small size and high polarity generally impart great plasticizing effect on polymeric systems (Cao et al., 2009).

In the efforts to improve the utilization of agricultural residues and decrease the accumulation of non-degradable plastic waste, the usage of a viscous liquid obtained from liquefaction of low cost, available and almost discarded biomass resources for film production is an interesting emerging field. In this regard, it is convenient the incorporation of biomass into macromolecular formulations due to the possibility of increasing the biodegradability of the final product. The novelty of this work is to open new fields of utilization for liquefied products made of raw materials with lower added value and evaluate their capability as main ingredient for film elaboration. Up to date, liquefied products have been mainly evaluated as precursors in PU synthesis. In that sense, this work provides preliminary basic technological information for extending the applications of liquefied products to polymer processing area for bioplastics development in agricultural applications.

In this context, several lignocellulosic residues (corn residues, vine shoots and blueberry tree pruning) generated in agricultural Chilean activities have been subjected to study. The aim of the present study was to evaluate the physico-chemical characteristics of liquefied products with respect to their film forming capacities and properties. Liquefied products and films were evaluated by different instrumental techniques and standard procedures.

## 2. Materials and methods

### 2.1. Materials and chemicals

Four types of residues generated in Chilean agricultural activities have been considered as renewable raw materials in this study. Corn cob (CC) and corn stover (CS) were collected after the harvest of maize (*Zea mays* L.) in O'Higgins region (Central Chile). Vine shoot (VS) of Muscat of Alexandria variety obtained from pruning of grapevine (*Vitis vinifera*) and blueberry shoot (BS) after blueberry trees pruning (*Vaccinium corymbosum* L.) were both obtained from cultivars from Bío-Bío region (southern portion of central Chile). All types of residues evaluated in this work were oven dried at 60 °C up to a moisture content about 2–4% (determined by dry weight in oven at 103 °C until constant weight) and milled in a commercial grinder to obtain particles and then sieved to the particle size of 0.3–0.6 mm (No. 30–50) and preserved at room temperature prior to analysis.

Polyethylene glycol (PEG) with average molecular weight ( $\bar{M}_w$ ) of 400 Da and glycerol (G) were used as solvents for liquefaction reaction. Sulfuric acid (SA) 96% was used as catalyst. Liquefied products as main polymer matrix and soluble (in water at 25 °C) potato starch (S2004 Sigma) were used for film formulation. Glycerol

(99.5% purity, Merck) was used as plasticizer. Apparent viscosity of starch pastes within the temperature range of 60–20 °C determined at constant shear rates is provided in Appendix A. All chemicals were of reagent grade.

### 2.2. Agricultural residues composition

The chemical composition of the raw materials was determined following standard methods and procedures found in the literature: ash content (TAPPI T211 om-93), lignin (TAPPI T222 om-98) (TAPPI, 2007); holocellulose (Wise et al., 1946),  $\alpha$ -cellulose and hemicelluloses content (Rowell, 1983). All determinations were performed at least three times. Means and standard deviations were reported.

### 2.3. Liquefaction of agricultural residues

The liquefaction reaction was carried out in a 250 mL neck flask reactor equipped with mechanical stirrer, temperature control and condenser. The liquefaction conditions were the following: weight ratio PEG:G:SA of 80:20:3, reaction time: 60 min; reaction temperature: 180 °C. A ratio of 0.25 of mass/liquefying solvent (w/v) was selected for the experiments with all raw materials. The experiment conditions (temperature, time and mass/solvent ratio) were selected according to adequate values found in previously published studies for several lignocellulosic agro-industrial wastes with similar physico-chemical composition (Briones et al., 2012). The mixture of polyethylene-glycol, glycerol and small quantity of sulphuric acid was placed into a reactor, heated to 180 °C. Then, the oven dried agricultural residue was added gradually under stirring and was held at this temperature during the reaction time. After a preset time, the flask was immersed in cold water to quench the reaction. The reaction mixture was diluted with acetone. The resultant dilution was filtered to separate the solid residue from the liquid fraction. The liquefied product was obtained from liquid fraction by the removal of acetone with a rotary evaporator under reduced pressure at 50–60 °C.

The solid residue was washed with acetone, dried at 105 °C for 12 h in an oven and weighed in order to determine the percentage of unreacted substrate. The extent of liquefaction conversion was gravimetrically evaluated on the basis of the unreacted raw material. The liquefaction yield ( $\eta$ ) was calculated as the weight percent based on the starting sample material by the following equation:

$$\eta = \left[ 1 - \frac{M}{M_0} \right] \times 100$$

where  $M_0$  is the mass of initial dry agricultural raw material and  $M$  is the mass of the residue insoluble in acetone obtained after the liquefaction reaction.

### 2.4. Characterization of liquefied products

With the aim to study changes in the chemical structure and corroborate the successful of the liquefaction reaction, liquefied products elaborated and their constituents were characterized by attenuated-total reflection infrared (ATR-IR) spectroscopy by direct transmittance in a single-reflection ATR System. Infrared spectra were recorded on a PerkinElmer Spectrum Two Fourier Transform Infrared Spectrometer. Each spectrum was recorded over 20 scans in the range from 4000 to 800  $\text{cm}^{-1}$ , with a resolution of 2  $\text{cm}^{-1}$ .

The pH was determined in water by a procedure similar to the methods used for wood or soil as follows: a mixture of 1 g of the sample of liquefied product and 50 mL of water was stirred, and the pH of the water was recorded on a calibrated pH meter (PC510-Oakton).

Measurements of viscosity of liquefied products obtained after acetone evaporation were carried out at 25 °C by using a digital

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