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Non-food Grade Biopolyols Containing High Lignin Content for Rigid PU Biofoams

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ABSTRACT

This paper presents the continuation of the development of renewable and non-food grade biopolyols containing lignin for the production of rigid PU foams. The new development of the biopolyols containing high content of lignin and its effect on the opening cell foams will be reported. The foaming ability as well as the characteristic and performance of the obtained biofoams in terms of density, cellular morphology, opening cell content, mechanical properties and thermal conductivity will be presented. The results demonstrate lignin can be used at higher contents in the biopolyol for the production of insulation foam if the modification and formulation are appropriate.

INTRODUCTION

Lignin is available in large quantities as a byproduct of the pulp and paper plants and recently the cellulosic ethanol plants. Lignin is the second most naturally abundant biopolymeric substance after cellulose; the natural polymer makes up to 40% of forestry and up to 30% of certain lignocellulosic materials in agricultural residues [1, 2]. Lignins obtained under these processes undergo significant structural changes and are no longer identical to their original native structures [3-6]. Due to its complex nature and undefined chemical structure, the industrial applications of lignin are rather limited. Presently lignin is utilized almost exclusively as fuel to power the evaporators of the chemical recovery processes and liquor concentration system of pulp mills [7].

In general, lignin is an amorphous, highly branched polyalcohol-phenolic macromolecule of complex structure. It contains significant amount of aliphatic hydroxyl group and if these groups are accessible lignin should be an interesting biopolyol for the production of polymer products including polyurethane (PU). However, the main question is how much one can access this hydroxyl groups in its complex structure.

In the previous publications the potential of a forestry Kraft lignin for substituting polyols in PU and rigid PU foam production and the influence of lignin on the formation and properties of the PU products have been briefly reported [8, 9]. This paper presents new data results on the formulation development of rigid PU foams containing higher lignin content. In this work demonstrate how lignin can affect an opening cell rigid PU foam.

EXPERIMENTAL

Aldrich's organosolv lignin was used in this study. It was dried at 60°C under vacuum for at least 4 hours prior to use. A proprietary polyol blend was prepared from a mixture of commercial polyester and polyether polyols. Surfactant and foaming agent were obtained from Evonik Industries and Honeywell, respectively. A catalyst and co-catalyst were supplied by Huntsman and Aldrich. Rubinate M, a mixture of Methylendiphenyldiisocyanate (isomers and homologues) and Diphenylmethane 4, 4'- diisocyanate, was kindly provided by Huntsman.

Lignin was dissolved into the polyol blend by a proprietary method. The obtained lignin-polyol mixture (so-called biopolyol) was mixed with catalyst, additives at room temperature then with isocyanate to form rigid foams in the lab scale.

Nikon Eclipse optical microscope (OM) was used to observe the solubility of lignin into the polyol. The viscosity of polyol-lignin was measured on Brookfield DV-E Viscometer. Foaming characteristic of the biofoam was evaluated on the Format Messtechnik's Foamat Foam Qualification System. The morphology of the PU foams was observed on the surfaces coated with a gold/palladium by scanning electronic microscope (SEM) JEOL JSM-6100 SEM at a voltage of 5 kV. Opening cell content and density of the foams were measured on the HumiPyc-InstruQuest according to ASTM D6226. Thermal conductivity of the foams was also measured on the LaserComp Fox304 according to ASTM C1045. Compression properties of the foams were measured on the Instron machine according to ASTM D1621 at ambient atmosphere, room temperature and 50% relative humidity.

RESULTS AND DISCUSSIONS

By using the appropriate mixing method, lignin is highly dissolvable in the polyol blend as seen in Figure 1. It indicates that the lignin chemistry, the system thermodynamics, and the proprietary blend formulation and technique are favorable for miscibility. The solubility is very stable after 6 months as no phase separation could be obviously observed (Figure 2).

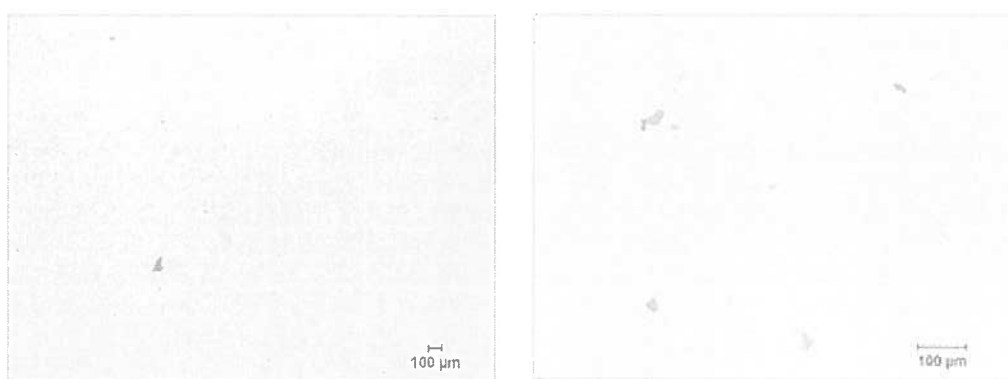


Figure 1. OM image of lignin-polyol



Figure 2. Photo of lignin-polyol after 6 months of storage at room temperature

Figure 3 illustrates the effect of lignin and its concentration on the foaming process of the rigid PU foams using exactly the same formulation. First, the temperature of the PU-lignin biofoams is rising during the foam formation due to the exotherms of the chemical reactions of isocyanate with polyol, lignin, water and itself. There is noticeable difference between the samples with and without lignin, and also its concentration. In general the presence of lignin slow down the rising temperature of the system indicating it induces the chemical reactions and the higher the lignin content the greater the effect. However, the maximum temperature of the biofoams is superior to that of the reference foam. The mechanism of these effects remains unclear and further investigation is necessary.

The foam rising is strongly related to the chemical reactions that release the exotherm and also the increase of molecular weight (or viscosity) of the system. If the chemical reactions take place too slow the temperature and viscosity of the system will also increase very slowly. The too high rising temperature can cause cell collapse thus foam collapse. Due to those reason the biofoamd containing lignin cannot raise at the same level as the reference. The higher is the lignin content; the lower the rising level. The catalysts, surfactants, blowing agent and isocyanate content were optimized for the reference foams and not for the biofoam so it is necessary to optimize the formulation as reported in the previous publication [10].

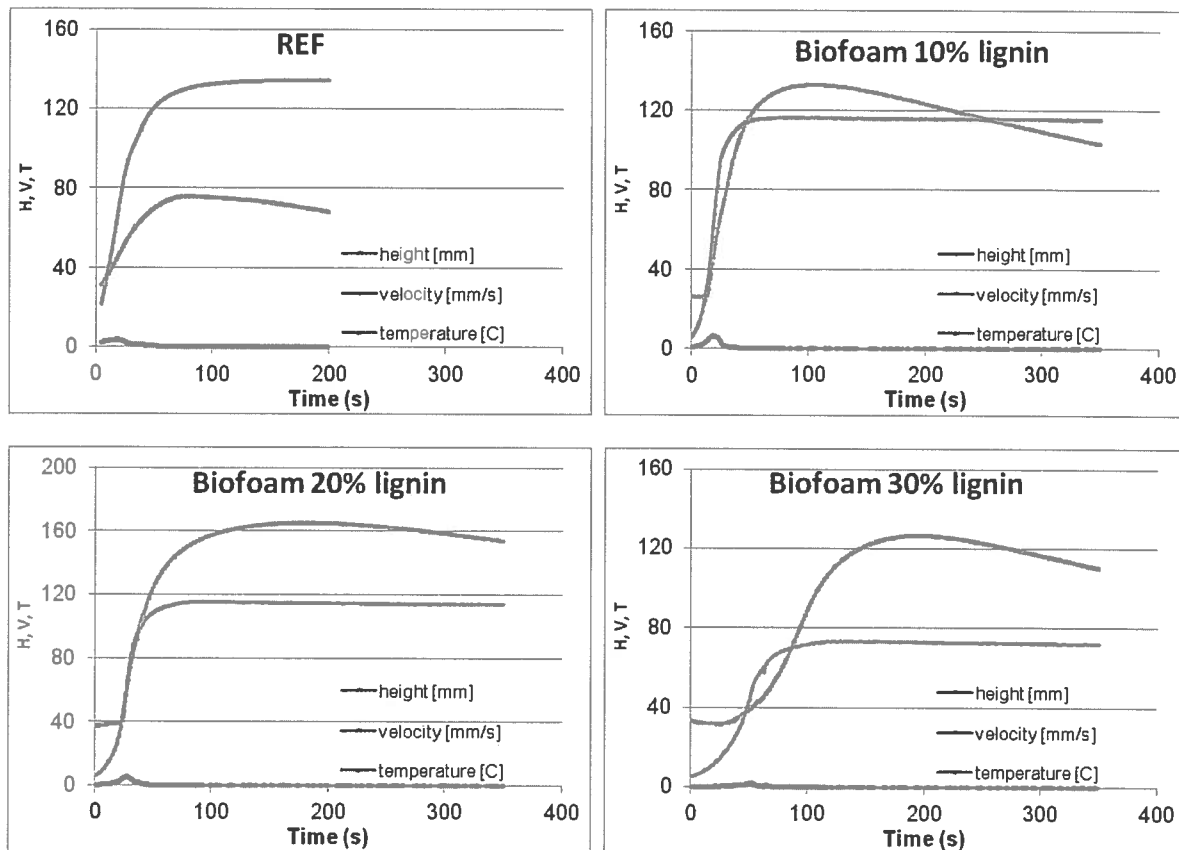


Figure 3. Foaming characteristic of the biofoams with Foamat

In order to shed some light on the behavior of lignin in the foaming as discussed above, different hypotheses can be proposed. Among them the alkali or acid residue in lignin can be one of the most likely causes and was validated. It is difficult to measure precisely the real pH of lignin because they are not soluble in water so the alkali or acid remains inside lignin particles cannot be easily to be detected. The experiment was designed to allow the system to have very mild acid or alkaline environment in order to investigate such effect. Figure 4 illustrates the foaming characteristics of the foam under mild acid and alkaline environment. The presence of either mild acid or mild alkali has affected significantly the foaming process, especially under acid environment. The presence of the strong acid such as acid sulfuric used to precipitate lignin from black liquor would poise the amine based catalyst by reacting with amine to form onium ion. Further experiments are necessary to understand more in dept of this effect.

SEM images of the foams are shown in Figure 4. In general, the cellular structure of the foams is identical in both cases, with and without lignin, which consists of regular round cells. However, the cellular size of the biofoams is much finer with the presence of lignin. The cell collapse to form big cells becomes evident for the biofoam containing 30wt% lignin. There is no lignin particles could be found in the biofoams. One could speculate that lignin has been participated into the PU network structure.