



Flexible polyurethane foams green production employing lignin or oxypropylated lignin



Jacopo Bernardini^a, Patrizia Cinelli^b, Irene Anguillesi^a, Maria-Beatrice Coltelli^a, Andrea Lazzeri^{a,*}

^a Department of Civil and Industrial Engineering, University of Pisa, Largo L. Lazzarino 1, 56126 Pisa, Italy

^b National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti, 9, 50121 Firenze, Italy

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ABSTRACT

An innovative and green chemistry synthetic approach was developed in order to employ lignin for the production of flexible polyurethane foams. Soda lignin and oxypropylated soda lignin were tested and compared. Glycerol and PEG 400 were used as polyol fractions for lignin liquefaction by microwave irradiation, which represents a novel green processing technique. The samples were produced with the “one-shot” technique, using two types of chain extenders in combination with liquefied lignin: castor oil and polypropylene glycol triol. Water was used as a single natural blowing agent, and polymeric diphenylmethane diisocyanate (PMDI) was employed as the isocyanate fraction. The work was carried out keeping the NCO/OH less than one hundred, thus enhancing the flexibility due to a lower crosslinking degree; all the foams were produced in free and controlled expansion. Two of the most efficient chain extenders were individuated thus introducing flexible chains into the macromolecular structure that can reduce the glass transition temperature of the materials and therefore generate foams with higher flexibility. The properties of the produced foams were compatible with the technical requirements for applications in packaging and for the production of the interior part of car seats.

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1. Introduction

Polyurethanes (PUs) are an important class of polymers synthesized by means of a polyaddition reaction between polyols, such as polyhydric alcohols and polyisocyanate that form urethanic linkages. These polymers are very versatile because they present structures ranging from rigid to flexible and are commonly used in various forms such as foams, elastomers, adhesives and many others, therefore they have a wide range of applications, i.e. automotive seating, furniture, and packaging and medical devices. Polyurethanes are also widely used as thermal insulators

in many industries such as footwear, construction, electronics and many others. Actually, common polyols employed to produce polyurethane foams are petrochemical in origin and, due to the escalation of crude oil prices, the cost of polyurethane reactants steadily increased, thus sparking interest in the quest for renewable sources.

Flexible PU foams are blocks of copolymers whose elastic properties depend on the phase separation between hard and soft domains. Hard blocks are rigid structures that are physically cross-linked and give the polymer its firmness; soft blocks are stretchable chains that give the polymer its elasticity. Therefore, polyurethane foams can be customized by adapting the composition and the ratio of these blocks.

Polyurethanes can be synthesized by using renewable sources as polyols, such as vegetable oils, by replacing

* Corresponding author. Tel.: +39 050 2217807; fax: +39 050 2217866.
E-mail address: andrea.lazzeri@unipi.it (A. Lazzeri).

petrochemical polyols partially or totally. Since the 1960s, a wide range of vegetable oils have been considered for the preparation of polyurethane; the most important ones are highly unsaturated, such as sunflower, palm, rapeseed and mainly castor and soybean oils [1–3].

Several attempts were made in order to use lignin as a novel and appropriate renewable feedstock, thus superseding petrochemical phenols and overcoming the idea that it is a waste and a low value by-product of wood pulping [4,5]. The use of lignin as such, or after appropriate treatments, was extensively investigated to prepare polyesters and polyurethanes exploiting its phenolic and aliphatic hydroxyl groups [6,7].

Lignocellulosic biomass is composed mainly of three chemicals: cellulose, hemicellulose and lignin, and its composition varies with the source and type of biomass. Lignin is an aromatic complex polymer that is highly branched and based on subunits of alcohol 4-hydroxycinnamyl (*p*-coumaryl alcohol) having methoxylated derivatives in 3- (coniferyl alcohol) and 3,5-positions (sinapyl alcohol) [8]. Lignin has a molecular weight of about 3000–7000 Da, an OH number of about 1000–1500 mg KOH/g, and a methoxy group content of about 13–14%.

There are many different types of lignin, whose nature depends on the different preliminary treatments that they have undergone and on the different types of wood [9]. Lignin is mainly isolated from wood pulping and papermaking operations, but only a small amount (1–2%) is recovered and employed as feedstock to produce other chemicals [10,11]. These pulping treatments provide fragmented lignin, thus enhancing its reactivity due to lower molecular weights and higher solubility in organic solvents. Soda lignins are sulphur-free and for this reason are considered as being closer to natural lignins; these lignins are mainly obtained from non-woody plants.

Many studies were carried out over recent years in order to use various lignins in polymeric synthesis. In this sense, Hatakeyama's group dissolved several lignins, such as Kraft, organosolv and sulphonate, into oligoether diols to obtain the polyolic mixture. By using the macrodiol as both the solvent and a comonomer, they improved the reactivity of lignin OH groups [12], and the introduction of flexible oligoether as spacers within the polymer chain reduced the network stiffness of the isocyanate. Also semi-rigid polyurethane foams, developed for housing insulation, were prepared by means of using lignin polyolic molasses, by controlling the apparent density, and by changing the mixing ratio between lignin and polyethylene glycol [13].

Oxypropylation of biomass was widely studied and is presently accepted as a method for improving the functionality of lignin [14–16]. A schematic pathway is reported in Fig. 1.

Glasser and his co-workers have modified lignins by using different conditions of high temperatures and pressures [17], allowing for further investigations on it in recent years [18].

The oxypropylation process allows to free the phenolic groups of lignin from steric hindrances and to obtain a lignin-based liquid polyol with lower glass transition temperature compared to the starting powder. It is a green

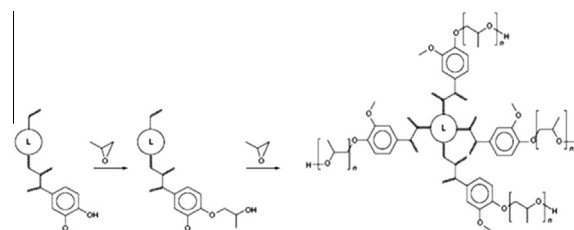


Fig. 1. Schematic pathway for the oxypropylation process of lignin.

process because it does not need further steps involving solvents and other by-product removal, nor is there the need for separation or purification steps in order to recover the final polyol mixture [19]. In this sense, the purpose of oxypropylation is to increase the lignin functionality for synthesizing polyurethane foams [20].

Many studies of oxypropylation were also carried out on renewable sources in order to produce low-cost natural polyols. Several biomasses such as cork [21], chitin and chitosan [19], and sugar beet pulp [22] were considered.

Currently, commercial lignins are not used in the industrial production of polyurethane foams due to the high viscosity of lignin-based polyols combined with a high temperature and very long reaction times; the extended structure of the lignin macromolecules must be fragmented before the employment in polyurethanes preparation. This process was defined liquefaction as the solubility of lignin was modified thanks to the occurring of fragmentation. Usually the reported methods consist in the use of proper solvent and heating. Microwave treatment can be an effective alternative because it is able to heat the core of the system. The microwaves were carefully studied to degrade hazardous compounds [23] and subsequently this treatment was tried on lignocellulosic biomasses [24–26] in order to obtain liquid polyols with shorter reaction times. This approach was tried on commercial lignin and the final mixture contained a higher amount of phenolic OH groups and a lower amount of methoxy groups, thus improving the system reactivity [27].

Microwaves are able to penetrate and heat the present reaction medium, thereby reducing reaction times from hours to minutes; furthermore, when heating with microwaves there is a faster increase in temperature and a lower thermal degradation of reagents than traditional heating systems, thus being compatible with a green chemistry approach.

In previous research [28], the authors produced polyurethane soft foams from kraft lignin, achieving a promising quality of foams in terms of density and mechanical properties. It resulted interesting to investigate lignin produced using different processes and modified lignin in order to achieve optimized properties. Thus the present work was focused on the production of flexible polyurethane foams from commercial soda lignin and commercial oxypropylated soda lignin by adopting a green synthetic pathway. Two chain extenders were used to produce flexible foams in combination with liquefied lignin: polypropylene glycol triol (PPG triol) and castor oil; polymeric diphenylmethane diisocyanate (PMDI) was employed as

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