



Research paper

Polyurethane foams produced from pyrolysis oil – Production and possible application



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ABSTRACT

Rigid polyurethane (PU) foams are widely used for instance in building insulation. Two component systems comprising of a polyol as component A and a diisocyanate as component B are generally applied. Both components are produced from fossil oil resources. The liquid products from fast pyrolysis of biomass contain a large variety of organic compounds with –OH functional groups. This gives rise to the idea to substitute the polyol component in PU foams with such biomass based intermediates. Pyrolysis condensates derived from woody and herbaceous biomass were dried and samples of PU foams were produced with varying amounts of condensate substituting the polyol component. Especially the foams made from condensates produced from straw showed good insulation properties, which were expressed as low thermal conductivity. Here, with a substitution degree of 80% a thermal conductivity of $0.0283 \text{ Wm}^{-1}\text{K}^{-1}$ was achieved, which was 8% lower than for the foams produced from commercial components ($0.0308 \text{ Wm}^{-1}\text{K}^{-1}$). Preliminary results for the measurement of compressive strength indicated that the required value of 150 kPa can easily be achieved, especially with a high degree of substitution. These results show a high potential for the application of bio-based intermediates in the building sector. Further research on other properties is necessary, but the main requirements for thermal conductivity are already met without optimization of the catalyst/stabilizer system.

1. Introduction

Polyurethanes (PU) are one of the most widely used polymeric materials in the world. One of the most important commercial polyurethane product is polyurethane foam (PU foam), which is commonly classified as flexible, semi-rigid or rigid, depending on its mechanical performance and core density [1]. Rigid polyurethane foam is one of the most important insulating materials used in the construction industry today, because of its excellent combination of low thermal conductivity and proper mechanical properties [2]. PU foams are polymers formed by a condensation reaction between isocyanates having more than one reactive isocyanate group per molecule and alcohols having two or more reactive hydroxyl groups per molecule (see section 2). Similar to other polymeric materials, also polyurethane

industry strongly relies on fossil resources, as the main feedstocks used in polyurethane products synthesis (isocyanates and polyols) are obtained mainly from petroleum. Due to environmental concerns great efforts are made to find renewable substitutes for these raw materials. One of the promising substitutive resources is biomass as the only renewable carbon source. Many researchers have shown that the polyols derived from biomass-based materials, such as palm [3], soybean [4], wheat straw [5], corn stover [6] and sugarcane bagasse [2] have suitable characteristics (e.g. hydroxyl numbers, viscosities, molecular weight) for making polyurethane foams with comparable properties to conventional polyurethane foams. One of the promising methods to make use of residues from forestry and agriculture and to produce biomass-based oil is pyrolysis [7]. During pyrolysis, 3 products are formed: a solid residue called bio-char, a liquid fraction called pyrolysis

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condensates and permanent gases [8]. Pyrolysis is attractive due to the advantages of the produced bio-oil, which contains valuable liquid chemicals. Compared to slow pyrolysis, fast pyrolysis is the preferred process for obtaining bio-oil, as it leads to a relatively higher liquid yield instead of solid yield [9]. However, the target products for polyurethane manufacturing containing the functional hydroxyl groups like sugars, phenols and aldehydes make up only smaller part in the conventional pyrolysis condensates. Furthermore, the high water mass fraction and low pH value of the primary condensate also hinder the direct use of it [10]. Therefore, the target components must be concentrated and water and acids have to be removed. A staged condensation of the pyrolysis condensates provides the possibility to obtain the target products with higher concentration in certain condensation stages [11,12].

Rigid polyurethane foams were produced within the scope of this study with varying amount of pyrolysis condensates replacing partially the polyol component and the main properties with respect to foam application as building insulation - thermal conductivity and compressive strength - were measured and compared to commercial product samples.

2. Theory

The basic reaction behind the production of polyurethane foams, irrespective of rigid or soft foam production, is the addition of an isocyanate and an alcohol according to Fig. 1 to form the urethane group between two organic structures R and R'. To form polymers with high chain lengths monomers are used that have active groups at both ends of the molecule. As the addition reaction already starts at room temperature, molecules with mixed active groups (one isocyanate and one alcohol group) are avoided and two separate monomers with either two hydroxyl groups (component A) or two isocyanate groups (component B) are produced and stored separately.

In PU industry, different molecules are used bearing the reactive isocyanate group. Molecules having aromatic structures are usually used for the production of rigid polyurethane foams that are intended for the later use as building insulation, because they are more flame resistant and thermally stable than bifunctional diisocyanate molecules with a linear hydrocarbon backbone [13]. For this study Methylene Diphenyl Isocyanate (MDI) was chosen for convenience. Unfortunately, MDI (Fig. 2, top) is solid at room temperature. Its polymeric form PMDI (Fig. 2, bottom) with typically around 6 phenylene groups is liquid at room temperature and therefore easier to process.

As alcohol component two- or polyfunctional polymers with medium chain length are used. These polymers can either be esters (Fig. 3, bottom) or ethers (Fig. 3, top), whereas ethers usually are cheaper compared to esters [13]. If the ethers are produced from the polyaddition of ethylenoxide or polycondensation of ethyleneglycol Polyethyleneglycol (PEG) is formed, which is shown in Fig. 3 (top). Such dialcohol was used in this study.

In order to produce a foam instead of a hard, solid block, it is necessary to generate nucleating bubbles within the reacting mixture. Such blowing or foaming action can be attained by using either or both of the following [14]:

- a physical blowing agent (e.g. Pentane or hydrofluorocarbons), usually a solvent with low boiling point which evaporates off by the

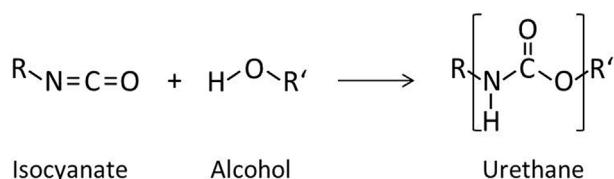


Fig. 1. Reaction scheme of urethane formation.

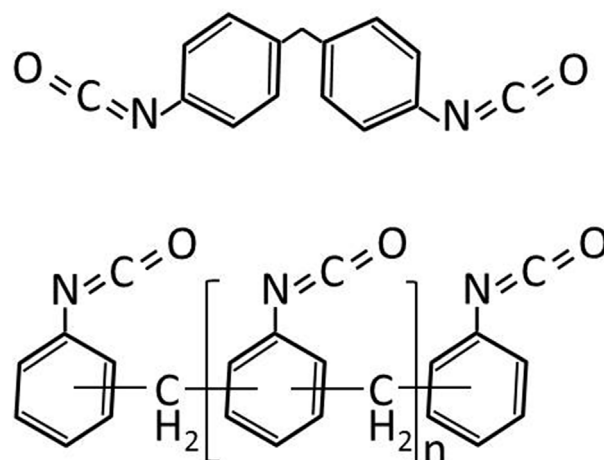


Fig. 2. Chemical structure of Methylene Diphenyl Isocyanate (MDI; top) and Polymethylene Diphenyl Isocyanate (PMDI; bottom).

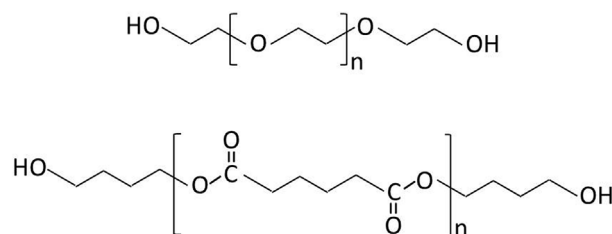


Fig. 3. Chemical structure of Polyether-dialcohol (top) and Polyester-dialcohol (bottom).

heat of the reactions, or

- a chemical blowing agent (water), which undergoes chemical reactions with the isocyanate to liberate a gaseous product (carbon dioxide).

As pyrolysis condensates naturally contain water, water was chosen as blowing agent. Following the reaction scheme shown in Fig. 4 water reacts with an isocyanate group by addition and subsequent CO₂ elimination, resulting in a primary amine. The evolving gas forms small bubbles which must be stabilized within the reacting mixture. To achieve this, a stabilizer is added to the mixture to prevent the coagulation of the primary bubbles [15]. Typically, silicone surfactants are used. These are available from several suppliers and its choice depends on the foaming agent used and intended application of the foam.

The foaming reaction between water and isocyanate group does not terminate the polymer formation, as the resulting amine can further react with an additional isocyanate group following the reaction scheme given in Fig. 5 to form a urea derivative.

Inevitable byproducts of biomass pyrolysis are carboxylic acids to different extend. These acids can react with both active compounds following the reaction schemes shown in Fig. 6: when reacting with the alcohol component (Fig. 6, bottom) esters are formed and with the isocyanate group (Fig. 6, top) amides are produced with the release of gaseous CO₂. As the acids in the pyrolysis condensates are usually monofunctional, these reactions terminate the chain growth on one side of either the alcohol or isocyanate component, which is unwanted. Therefore, a low acid concentration in the pyrolysis condensate is necessary.

In an earlier study Kazan National Research Technological University developed a basic recipe for the production of rigid polyurethane foam with partly substitution of the polyalcohol component A by pyrolysis condensate [16]. This basic recipe was also used in the present study (see section 3.2).

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