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The role of catalysis in the synthesis of polyurethane foams based on renewable raw materials

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ABSTRACT

In the last years growing attention is paid to environmental concerns with a special attention to bio- and renewable resources as feedstock for the chemical industry as well as to heterogeneous catalytic processes as tools for the elimination of wastes. This paper describes the results obtained in the application of vegetable oils stabilized through a selective hydrogenation process for the preparation of polyols and therefore in the synthesis of flexible polyurethane foams which are the most common and widely used among polyurethane materials. The influence of a different catalytic system on gelling and blowing reactions was studied and then properties of obtained foams were compared. It was found that the selection of catalytic system during preparation of polyurethane foams substantially influenced the properties of the final materials.

1. Introduction

Catalysis plays a fundamental role in industrial chemical transformations. More than 85% of industrial chemicals are made through catalytic processes since catalysts provide more energetically favorable reactions in comparison to non-catalytic ones, thus allowing the use of milder reaction conditions [1]. Catalysts have significant influence on the polymerization reaction mechanism e.g. free-radical, cationic, anionic and insertion polymerization. Among others, Ziegler–Natta catalysts as well as metallocene catalysts which have been successfully introduced in industry for the production of polymers for new applications, should be mentioned [2]. The right choice of the catalyst has a significant effect on polymer formation and on the time required for polymerization. Moreover, the catalyst determines the properties of obtained polymers such as polyurethanes which are manufactured by polyaddition reaction between di- or poly-isocyanates and two- or multi-functional polyols. Flexible foams are low-density cellular polyurethane materials, with limited and reversible resistance to compression. Among them, the most widely used are water-blown slabstock and molded flexible foams. Proper selection of catalyst formulation in the preparation of polyurethane foams influences the properties which are required for a number of applications in bedding, furniture and automotive industry [3].

The polyurethane market accounts for around 7% of the global polymer market [4]. Generally, polyurethanes can be classified into flexible foams (∼50%; furniture, mattresses, automotive seats), rigid foams (∼30%; insulation and structural materials), as well as coatings, adhesives, sealants and elastomers (∼20%; paints, binders, lacquers and elastomeric materials) [5,6]. From the chemical point of view, polyurethanes are obtained from a range of different reactions, including reaction between isocyanate (—NCO) and polyol (—OH) which gives 'urethane' groups (—NHCOO—). Polyurethane foam formation essentially consists of two reactions (Fig. 1). The first one is isocyanate–polyol reaction, known as the gelling one which forms the backbone urethane group. This reaction leads to the formation of a cross-linked polymer, since polyols with several hydroxyl groups are used. The secondary reaction of a urethane group with an isocyanate group to form an allophanate group is another possible way to further cross-link the polymer. The second one is isocyanate-water reaction, known as the blowing one which forms the carbamic acid which decomposes to give an amine and carbon dioxide gas in the form of bubbles. Next, the formed amine group reacts with another isocyanate group to give a disubstituted urea. The second part of the blowing reaction contributes to chain extend the aromatic groups of the isocyanate molecules to form linear hard segments. Another secondary reaction involves the formation of biuret and allophanate linkages which could lead to the formation of covalent cross-linking. The correct balance between these reactions is required since it controls the foam stability and allows to achieve foams with tailored physical properties. The catalysts used in the synthesis of polyurethane foams help to precisely control the relative reaction rates of the isocyanate with both polyol

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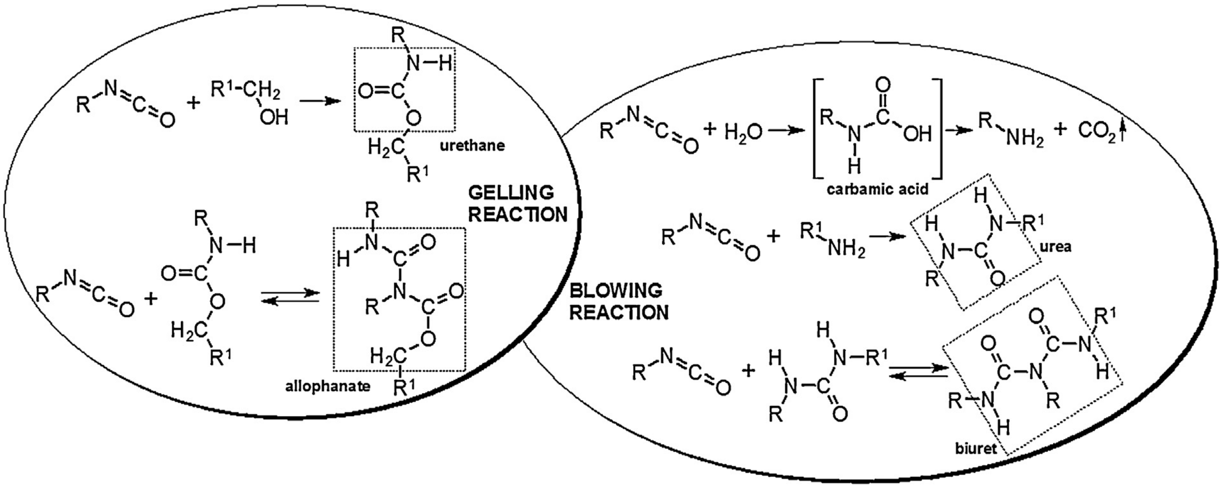

Fig. 1. Scheme of gelling and blowing reactions in the synthesis of polyurethanes.

and water. The imbalance between them can cause the foam collapse or formation of inappropriate cells that can be closed or opened prematurely [3,5,7–9].

There are mainly two types of catalysts used in polyurethane technology, i.e. amine catalysts and organometallics. Amine catalysts generally catalyze the isocyanate–water reaction better than the isocyanate–polyol reaction, while organometallics are considered as gel catalysts although they additionally influence blowing reactions [3,5]. The amine catalysts, especially tertiary amines, are the most common organic base catalysts in the synthesis of polyurethanes. One of the most commonly used tertiary amine catalyst is 1,4-diazobicyclo[2,2,2]octane (DABCO). It catalyzes both isocyanate–polyol and isocyanate–water reactions. One of the drawbacks of using tertiary amines is their offensive fish-like odor and high volatility. Increasing environmental concerns toward decreasing of emissions of volatile organic compounds (VOC) have contributed to the development of nonfugitive catalysts. Two mechanisms have been proposed to describe the amine catalyzed urethane formation (Fig. 2). The first mechanism proposed by Baker assumes formation of a complex consisting of a tertiary amine catalyst and an isocyanate, which is followed by the attack of nucleophile. On the contrary Farka postulated formation of urethane through protonation of the catalyst by interaction of the amine with a proton source (such as polyol, water or amine) to form a complex, which subsequently reacts with the isocyanate [3,8].

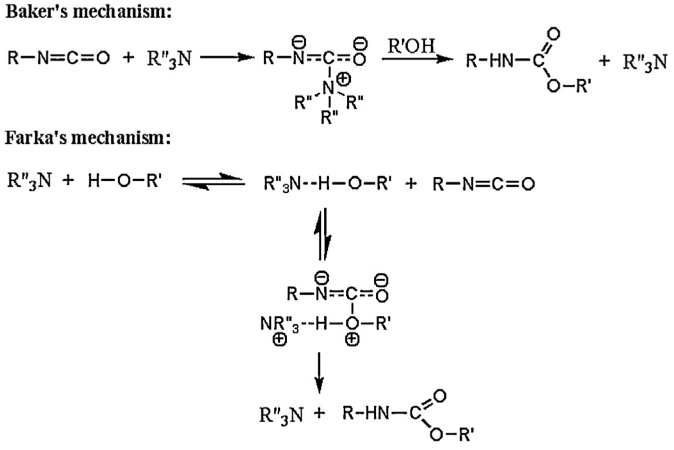

Fig. 2. Mechanisms of urethane formation catalyzed by amine [3].

The manufacturing of flexible polyurethane foams requires precise kinetic control over the above mentioned competing gelling and blowing reactions. If the blowing reaction is much faster than the gelling one, the cells will open too early, before reaching adequate viscosity. This will inhibit the formation of strong foam struts and foam will collapse. On the other hand, if the gelling reaction is faster than the blowing one, the formed polyurethane network will entrap the gas and suppress formation of bubbles, thus resulting in a foam with closed cells. Therefore, it is important to find a kinetic balance point for the foaming process [6,10].

The basis for sustainable economic growth is the need of environment protection. Production of flexible polyurethane foams requires a variety of chemicals and additives. At present, great importance in polyurethane industry is related to the application of vegetable oil-based polyols instead of petrochemical equivalents [11–18], as well as to the usage of non-volatile, reactive catalysts, since unreacted traditional amine catalysts create toxic vapors [19,20]. Our research was focused on two main issues, catalytic hydrogenation of vegetable oils into more oxidatively stable materials and the proper choice of catalytic system in the preparation of polyurethane foams. In this work, we will present the importance of application of catalysts in the synthesis of flexible polyurethane foams obtained by partial replacement of petrochemical polyether polyol with rapeseed oil-based counterparts.

2. Experimental

2.1. Materials

Rapeseed oil manufactured by ZT Kruszwica SA was used in the investigations. Glacial acetic acid (99.5 wt%), toluene (99.5 wt%), hydrogen peroxide (30 wt%), sulfuric acid (95 wt%), and diethylene glycol used in the synthesis of rapeseed oil-based polyols were purchased from the POCh Gliwice.

The foam formulations were prepared using: ROKOPOL M5000 having hydroxyl value equal to 36 mg KOH/g, molecular weight of 4800 g/mol and viscosity at 25 °C equal to 800 mPa s (trifunctional polyether polyol based on glycerine, PCC Rokita SA), vegetable oil-based polyols RDEG and HRDEG, TDI 80 (toluene diisocyanate 80/20, ZACHEM SA), DABCO DC 5950 surfactant (polysiloxane–polyoxyalkylene copolymer, Air Products and Chemicals Inc.) and catalysts (DABCO BL-11, DABCO 33-LV, DABCO NE300, DABCO NE1070, POLYCAT 15) from Air Products and Chemicals Inc (Table 1).