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Production of Polyurethane using Advanced Renewable Based Polyol: A Review

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Abstract

Traditionally, polyol used in the synthesis of polyurethane is derived from petrochemicals that are non-renewable. Due to the non-renewability of these petrochemical feedstocks, attention is now on renewable feedstock (vegetable oil) for the production of polyol for polyurethane synthesis. Since there are several vegetable oils available from which polyol can be derived, this paper reviewed the development in the last decade in the synthesis of polyurethane from different vegetable oil-based polyols. The review revealed that vegetable oils such as soybean oil polyol, castor seed oil polyol, and palm oil have been used in the production of polyol in the last decade and are more environmentally friendly. The review showed that the use of vegetable oils-based polyol in the production of polyurethane is economically and environmentally friendly. However, there are still different natural plant oils from which polyol can be derived in the production of polyurethane.

Keywords: Polyurethane; Polyol; Renewable; Vegetable oil

Introduction

Polyurethane is one of the most versatile polymers that have been used in a wide range of areas. Flexible and rigid foams, coatings, sealants, elastomers and adhesives being other common forms of applications [1]. Currently, the polyurethane industries are heavily petroleum dependent because its two major feedstock polyols and isocyanates are largely petroleum derived. Due to the concern over the depletion of petroleum resources, vegetable oils are materials which are highly adaptable to their circumstances [2]. Polyurethane materials created from vegetable oils such as rigid foams and cast resins have been used for some times in the last decade. Technologies to produce polyols from vegetable oils are economically competitive to petrochemical based polyols [3]. Raw materials from vegetable oils are important sources for polyol used in the production of polyurethane. However, as the oil crisis and global warming deepen, there are great interests in utilizing renewable sources as substitutes for petrochemical derivatives [4]. The resulting trends towards the use of more sustainable and environmentally friendly raw materials means that there is an excellent opportunity for polyols derived from renewable feedstock like the vegetable oils to partake in the polyurethane market [5]. During the past few years, a variety of chemical modifications of vegetable oils have been studied to derive multiple hydroxyl functional derivatives which are used as polyols in the polyurethane preparations [6]. In recent years quite a number of research and development works have been carried out for utilizing vegetable oils in wide range of applications, including polyols used in polyurethane. The most promising natural oils for the industrial development of bio based polyols are epoxidized soybean oil, castor oil, palm oil and canola oil [7-11]. They are materials which are having appropriate reactivity because of functional groups having more than two hydroxyl groups per molecule thereby can be used as polyols for polyurethane synthesis. There are also double bonds in the structure of vegetable oil which can be modified by hydroxylation [12]. Vegetable oils are excellent renewable sources of raw materials for the manufacture of polyurethane components such as polyol. To use vegetable oil-based polyol as a monomer for the preparation of polyurethanes, it should be suitably functionalized. The transformation of the double bonds of triglycerides of oils to hydroxyls and their application in polyurethanes are the subjects of many studies [13].

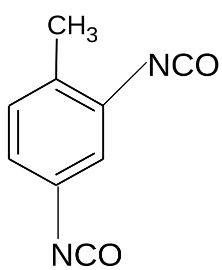
In general, Polyurethanes have been applied in various products such as thermal insulations and medical implants. The preparation of various types of polyurethane products has been extensively studied in recent years especially containing biomass–originated raw materials [14].

Polyurethane chemistry

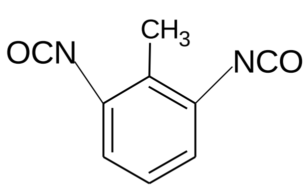
Raw materials: In polyurethane, the most important isocyanates, covering the majority of polyurethane applications are aromatic isocyanates: Toluene Di-isocyanate (TDI) and Methylene Diphenyl di-isocyanate (MDI). TDI is commercialized using a mixture of 2,4 and 2,6 isomers or 2,4 TDI as pure isomers.

The most common method of producing or making polyurethane are isocyanates and polyols. The isocyanates are produced by phosgenation of amines [15]. The reaction is usually completed in a chlorinated aromatic solvent. Some of the isocyanates used in polyurethane industries are

I. Toluene Di-isocyanate (TDI)

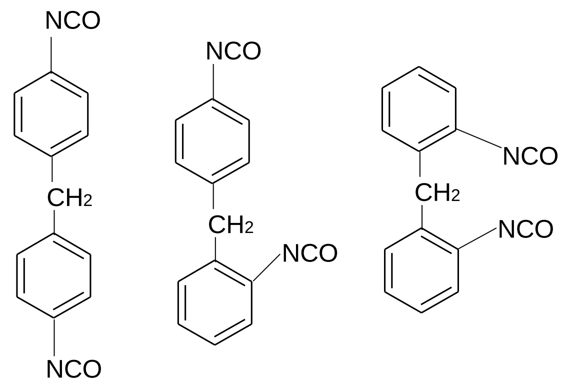


2, 4 -TDI



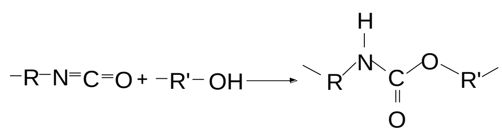
2, 6 –TDI

II. Methylene diphenyl di-isocyanate MDI

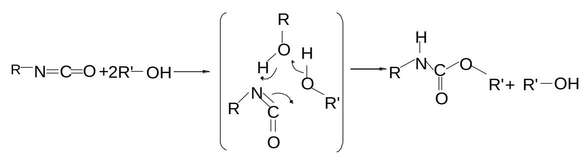


4,4 – MDI, 2,4 – MDI, 2,2 – MDI

These polyurethanes are produced by a stepwise polyaddition reaction from a polyhydroxyl compound bearing at least two hydroxyl groups and an isocyanate with at least two isocyanate groups as indicated in the general formula [16].



The mechanism of the reaction is a six-centered ring mechanism in which a proton is shifted from the H-active compound to the nitrogen atom of the isocyanate [17].



The reaction is either auto-catalytic, i.e. the free electron pair of the urethane nitrogen acts as the catalytic species, or it’s catalyzed. Catalysis to be used includes nitrogen compounds having at least one tertiary nitrogen, an organometallic compound, or Lewis acid. The frequently used catalysts in polyurethane formation are N, N-dimethyl cyclohexyl amine, N,N-dimethyl ethanolamine [18] (**TABLE 1**).

FIG.1. **Some physical properties of polyisocyanates.**

Designation	Formula	M. Wt. g/mol	B. Pt.(°C)	Density (g/cm^3)
2,4 -TDI	$C_9H_6O_6N_2$	174.2	121	1.2178
2,6 -TDI	$C_9H_6O_6N_2$	174.2	121	1.2271
4,4 -MDI	$C_{15}H_{10}O_2N_2$	250.3	208	1.183
2,4 -MDI	$C_{15}H_{10}O_2N_2$	250.3	154	1.192
2,2 -MDI	$C_{15}H_{10}O_2N_2$	250.3	145	1.188

Literature Review

V. Sharma *et. al*., 2008 synthesized various types of useful condensation polymers, such as polyurethanes, polyesters and polyether’s. As vegetable oil are one of the most readily available alternative renewable resources and the functional groups present in natural oil can be activated for condensation polymerization, they have converted natural oil into the polymer chain. They found various useful properties of polyurethane products for their widespread application [19].

Jalilian *et. al.*, 2008 synthesized and characterized a polyurethane networks from new soybean oil-based polyol and a bulky blocked polyisocyanate. For this they prepared a new soybean oil-based polyol with high functionality of hydroxyl groups and built-in (preformed) urethane bonds [20].

Javier Chavarro Gomez *et al*, 2021 prepare and characterizes polyurethane foams using palm oil-based polyol by mixing the palm oil polyol with either polyethylene glycol or diethylene glycol followed by a catalyst. A surfactant formed a pre-mixture, then PMDI was added and the reaction was allowed to proceed at room temperature with vigorous stirring [21].

Lise Maisonneuve *et al.* also made their research contribution in the production of rigid polyurethane foams from a soybean oil-based polyol. They used a commercial soybean oil-based polyol and a selected isocyanate (Polymeric methylene diphenyl diisocyanate), diethylene glycol was used as a chain extruder to avoid foam shrinkage. N,N-dimethyl cyclohexyl amine as the gelation catalyst was used with a Penta methyl diethylenetriamine as a gelation agent [22].

Raminda Kaur and Mukesh Kumar, 2020 used castor oil-based polyol (99%) and 4,4-diphenyl methane diisocyanate in the production of polyurethane through a condensation reaction where the reacting contents were heated to a temperature of about 230oC. The heating was carried out till the hydroxyl value of the oil (polyol) reaches 390 mgKOH/g-410 mgKOH/g [23].

Anda Fridrihsone *et al*., 2013 using rapeseed oil-based polyol, the PU samples were cast from a solution of 50% anhydrous toluene at a temperature of 20℃-25℃. The functional group ratio NCO:OH was 1.1. When the conversion of NCO groups reached 60%-70%, the solution was poured on polyoxymethylene support and left at a temperature of 70℃ for 2 h for conditioning. In preliminary tests for each series, the NCO group concentration was determined by using chemical analysis methods, and then NCO group conversion was calculated. After the conditioning, the PU films were left at room temperature for 3 days before film stress-strain determination. The obtained films had a thickness of 150 lm-250 lm [24].

Petrovic and co-workers studied polyurethane foams based on soybean oil. They prepared both Hydro Chlorofluorocarbon (HCFC) and pentane-blown rigid Polyurethane (PU) foams from polyols derived from soybean oil [25].

kaiwen Liang and Sheldon Q. Shi, 2010 prepared polyurethane foams by one-pot and free-rising method. They Weigh some known amount of the polyol, catalysts, surfactant and blowing agent (B-side material) using disposable plastic cups; Mix them with a mechanical stirrer at 3000 rpm for10 s~15 s; Allow the mixture to degas for 2 min; Rapidly add pMDI (A-side material) into the mixture and continue to stir for another 10 s~15 s at the same speed; Allow the foam to rise and set at room temperature for 24 hr. thoroughly mixed with B-side material before adding pMDI [26].

Different strategies have been used in order to synthesize polymers from vegetable oils

I. Direct polymerization of vegetable oils
II. Modification of vegetable oils and polymerization
III. Polymerization of oil-derived platform chemicals

Soybean based polymers

Soybean oils are biodegradable vegetable oil and available in bulk quantity. Natural soybean oil possesses a triglyceride structure with highly unsaturated fatty acid side chains. This unsaturation in these oils provides ideal monomers for the preparation of various polymers. Polymers derived from soybean oils have been investigated. Polymers from different soybean oils show different properties, and the cross-linking density of the bulk polymers affects their thermos-physical properties [27].

Castor oil polymers

Castor oil is a vegetable oil obtained from the castor bean of the castor plant. It is a triglyceride in which approximately 90% of fatty acid chains are ricinoleic acid. Oleic and linoleic acids are the other significant components. Epoxidized castor oil has been used for the preparation of Interpenetrating Polymer Networks (IPN). It is observed that the cross-linked IPNs from the epoxidized oil and adducts of tung oil with maleic anhydride had very good compatibility. The hydroxyl groups of epoxidized castor oil form hydrogen bonds with the carbonyl groups in tung oil. These hydroxyls are more reactive towards Tung oil adducts than epoxidized cottonseed oil. Styrenated castor oil and linseed oil can be prepared by the macromer technique. The copolymerization of dehydrated castor oil with styrene has been reported. A blend of dehydrated castor oil and epoxy resin and the miscibility of the blends of epoxidized dehydrated castor oil and poly (methyl methacrylate) has been reported [28].

Conclusion

These polyurethanes from plants oil have high strength as well as stiffness, environmental resistance, and long life. In recent years, plant oils have become the best alternative for petroleum-based polymers. However, it has become the main goal for researchers in the coming years to produce viable polymers from plant oil resources. These plant oils provide a large variety of options for the preparation of different polymers.

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