Research Article

Polyol and Isocyanate Production from Wastes According to Green Chemistry Principles

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Abstract

The need for renewable and sustainable resources is increasing like an avalanche every day in order to take measures against the decreasing oil resources on earth and the crises that will be experienced in the related industries. Lignin, a natural biopolymer, is abundant in terms of renewable resources. Nowadays, very intensive efforts are being made to evaluate the wastes of biological resources and to produce upcycled materials. In this study, we synthesised polyurethane by polycondensation reaction by obtaining lignin from corn cob wastes and chitosan from shrimp shells. The effects of temperature, pressure and time on the synthesis process were investigated and the optimum process conditions were determined. It was concluded that the production efficiency increased with the effect of catalyst and the water output rate improved accordingly. It is stated

that the adhesion process of polyurethane with metal cans is compatible with the adhesion process of polyurethane to be used in the filter sector.

Keywords: Polyol, isocyanate, polyurethane, green chemistry

1. Introduction

Polyurethanes (PUs), which are synthesised for use in many areas of industry using traditional methods, are obtained through reactions between polyol and diisocyanate. These materials are used for many purposes. They have an outstanding potential for use in a wide range of applications in the filter industry for protective layers, sealants, adhesives, coatings, thermal stability and strength [1]. For many years, both initiators that make up polyurethane have been produced from petrochemicals [2]. Due to their burden on the environment, the end of fossil resources and the increasing development of their current use, the search for alternative production processes and natural raw materials has accelerated [3]. Production according to environmentally friendly, green chemistry principles constitutes the most important task that we can contribute to the world heritage. Promising studies for this situation, which today's scientists are intensively thinking about, continue to increase. In recent years, the use of bio-sourced natural materials in the development of polyurethanes has been investigated [4-5].

In polyurethane production, there are concerns about the sustainability of raw materials based on natural materials such as oils, sugars and bio-based glycerol. Limited production areas, changing climatic conditions and dramatic reduction of water resources play a major role [6]. After the millennium, major plastics industry players have shifted from fossil-based polyurethane sources (pPU) to polyurethane from renewable and sustainable sources (gPU) [7]. The biggest challenge here is the production processes and extra pre-treatments. Soya bean oil, castor oil, cocoon oil, known as bio-polyols, are the most used materials in the production of gPUs [8]. Polyurethanes are derived from chemically modified triglycerides and fatty acids [9]. Isocyanates, another starting material of polyurethanes, are generally formed because of the reaction of phosphagen with compound containing amine group [10].

In the literature, there are no comprehensive studies to produce isocyanates from renewable sources [11]. Currently, there is no comprehensive study on the preparation of isocyanates from renewable raw materials. Besides the toxicity of the starting materials used, the biggest challenge is the limited petroleum resources [12]. In studies on the synthesis of polyurethane from natural materials, there are studies on the production of

both polyols and isocyanates as starting materials from vegetable oils, sugars or lignin [13].

There are various limitations and challenges to sustainability in the use of renewable resources, especially natural materials. Generally, the use of food-derived materials is also unsuitable for sustainability. Lignin, a natural polymer found in corn cobs, a lignocellulosic waste, has a significant potential for biobased PUs due to its hydroxyl groups and high mechanical strengths as well as its industrial usability as a by-product in some sectors. Another waste biomass, chitin obtained from shellfish, is a material that is used in chitosan production and thus in polyurethane production.

2. Materials and Methods

2.1. Materials

Kraft lignin (KL) obtained from lignocellulosic corn cobs and crustacean shrimp shells (KK) were supplied by Gülnaz, O., (Chemvirotech). Sodium hydroxide (0.1M), Iron (III) Chloride (150 mg), KOH (0.1 M) and Hydrochloric Acid (37%) were purchased from Sigma Aldrich at the highest purity available and used as received.

2.2. Methods

Shrimp shells were used in the synthesis of chitosan. The collected shrimp shells were washed with drinking water and dried. Then, shrimp shells were subjected to decalcification process. For this, they were pretreated with 1 N HCl acid. After decalcification, the shells were washed again with water and dried for the next step. The dried shells, which were dried and divided into smaller pieces, were reacted with protease enzyme for 72 hours for deproteinization process. Alkaline protease was preferred as protease enzyme here. The portion obtained after deproteinization was subjected to deacetylation for 8 hours at 80 °C by adding 1 M NaOH. The product obtained after deacetylation was colourised with acetone to obtain chitosan (Figure 1).

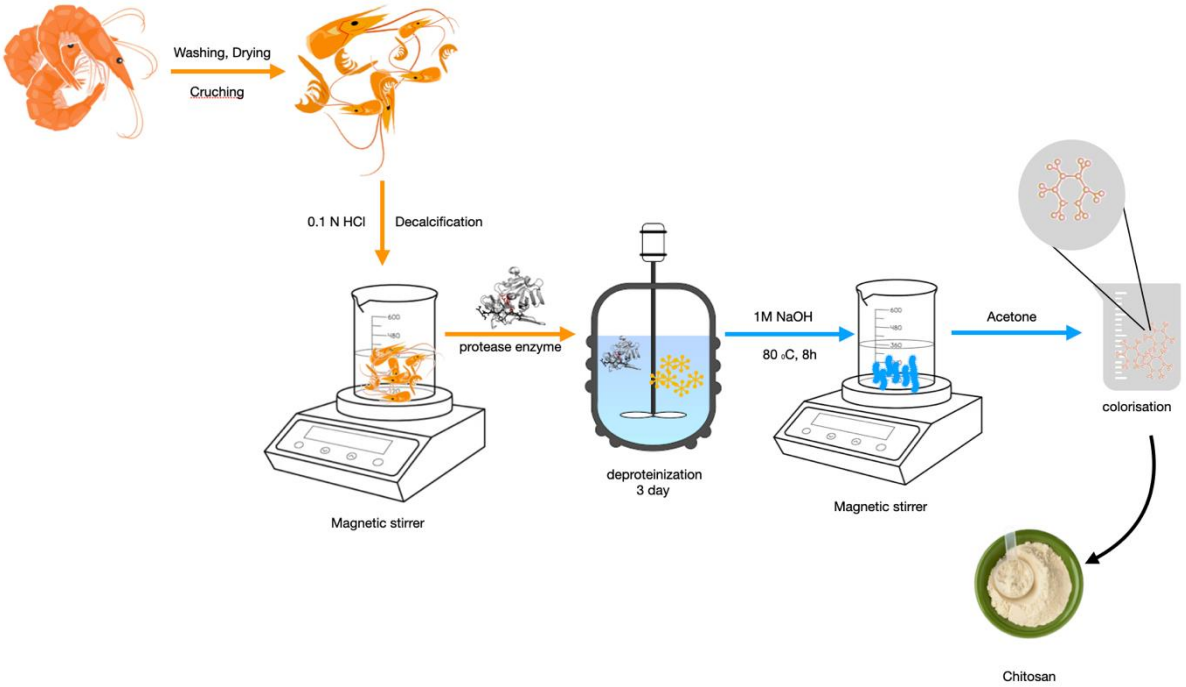


Figure 1: Preparation of chitosan from shrimp shell

Maize stalks with cellulosic content were collected to obtain lignin. They were subjected to drying process up to 90% dry matter content. The dried corn cobs were pulverised using a cooled and knife grinder. The obtained powder material (containing 6% dry matter) was mixed with 0.1 M NaOH solution at 80 °C for 8 hours on a heater with magnetic stirrer. The mixture was cooled to room temperature and the remaining solids were separated by filtration. The remaining liquid portion, called black liquor, was separated and taken into a beaker. It was precipitated by adding 5ml of the previously prepared 1M $FeCl_3$ solution. The precipitate was centrifuged and dried at 60°C to obtain lignin (Figure 2).

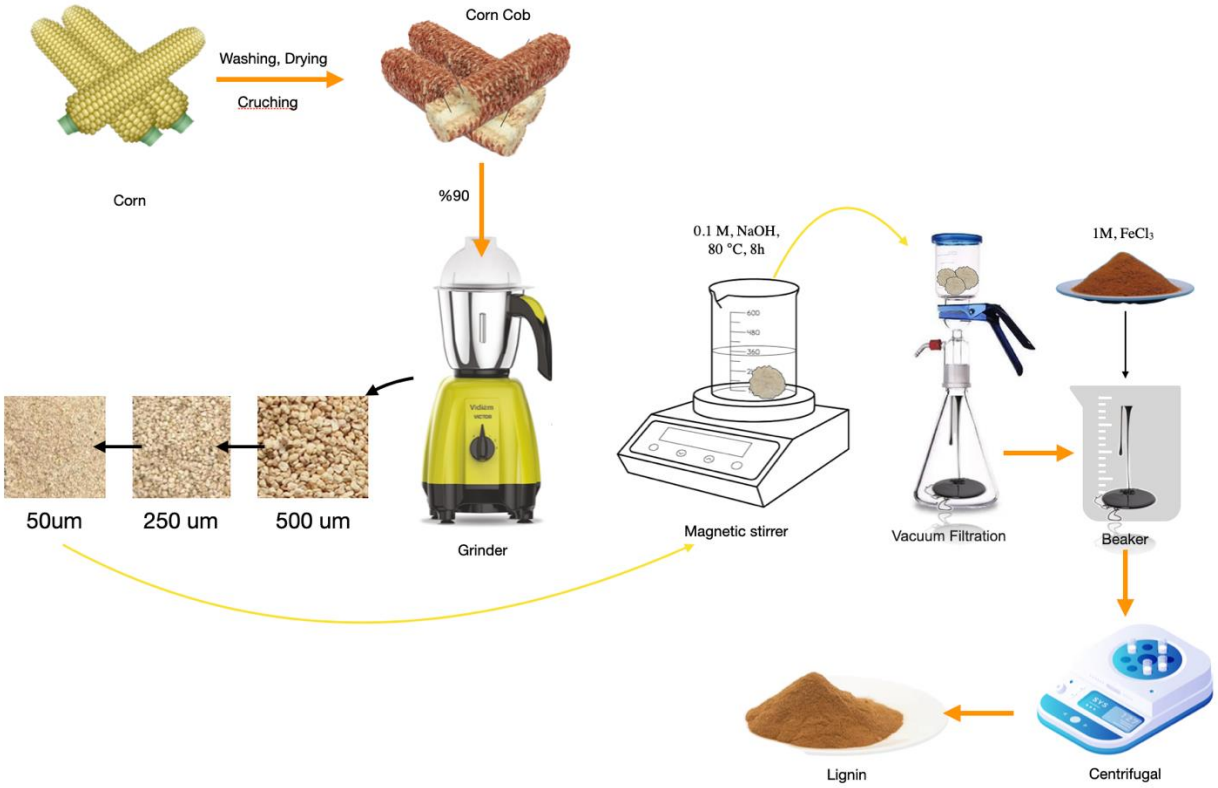


Figure 2: Lignin extraction from corn cob

For hydroxypropylation, lignin obtained from waste corn cobs was dried in a vacuum oven with nitrogen gas circulation at 55 °C for 12 hours. For this process, the hydroxypropylation steps given in the literature were followed [14]. For this process, 3 g of lignin was dissolved in 1.5 M 25mL NaOH solution with stirring. In the next step, 5 mL of propylene oxide was slowly added to a homogeneous lignin solution and stirring was continued. After it was brought to room temperature, dilute hydrochloric acid solution was added dropwise to adjust the pH and it was fixed between 10-11. Stirring was continued for 12 hours at room temperature under pH control. After waiting for precipitation, precipitation was performed again with HCl (pH 3). It was washed with distilled water under vacuum and filtered. The brown powder obtained was dried in a vacuum oven at 55 °C and stored. For the synthesis of biobased polyurethane, a three-step polycondensation reaction was carried out, firstly esterification, then polycondensation and finally chain extension. The main purpose of choosing this method is to facilitate the removal of by-products. In this way, control over the reaction conditions

is provided. As a result, a polymeric structure with the desired properties was obtained (Figure 3).

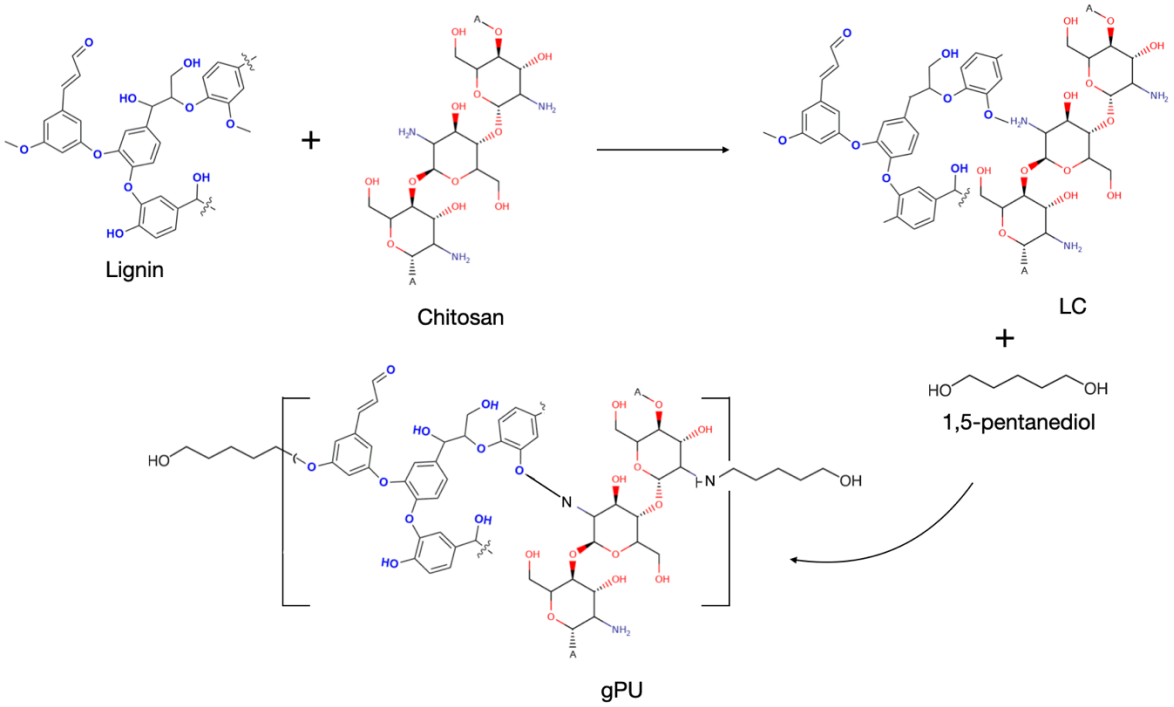


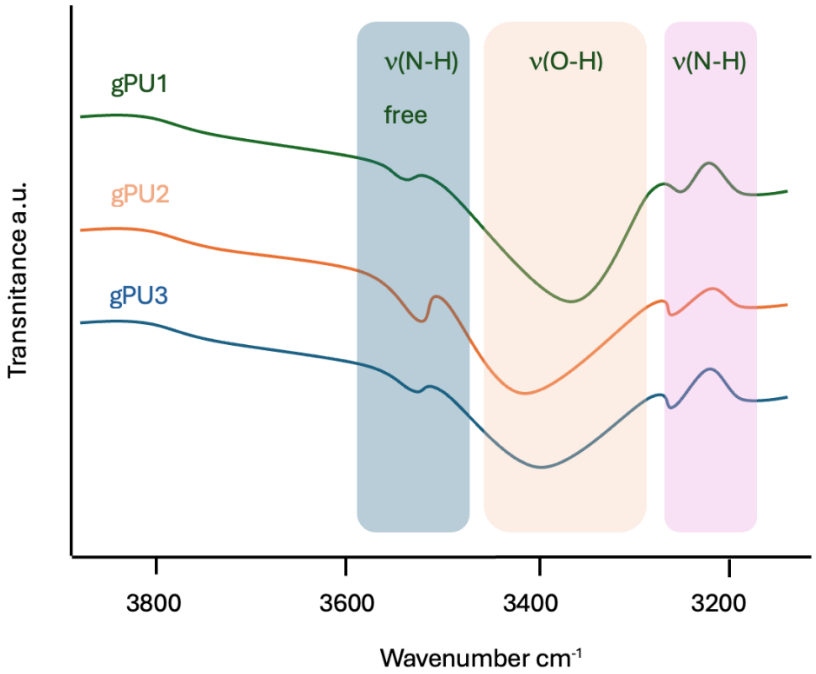
Figure 3: Polycondensation polymerization

In the polymerization reactor, KL and KK were weighed in 1,5/1 mole ratios and loaded into the reactor. The air was evacuated under 2 Pa vacuum to work in a vacuum-free environment. It was heated and stirred at 160 ◦C for about 2 hours under nitrogen gas. Then the temperature was increased to 200 ◦C and the stirring speed was kept constant at 300 rpm. For the most important step of esterification, pure water was completely removed. Foaming was prevented by adding 0.01 g of tin octoate catalyst to the medium. The vacuum was increased to 5.0 Pa to control the product formation during the reaction process and to remove water quickly. In the polycondensation process, the temperature was increased in a controlled manner up to 220 ◦C. Meanwhile, the stirring speed was increased to 500 rpm. After stirring for 1 hour at the same temperature, the temperature was increased to 230 ◦C and continued for another 30 minutes. The product obtained was preserved.

FTIR spectroscopy was used to determine the chemical structure of the obtained copolymer. FTIR spectroscopy was performed and interpreted with Schimadzu, IRXross brand and ATR (Gladi-ATR, Pike Technologies) technique. Spectra were collected in the 4000-400 cm^{-1} region with 4 scans and 4 cm^{-1} resolution.

3. Results

Fourier Transform Infrared Spectroscopy (FTIR) was used for the characterisation of the synthesised polyurethane. The polymerisation of gPU obtained in Figure 3 was followed by FTIR-ATR spectroscopy. The spectra of gPU are shown in Figure 4 to understand whether there is a polymerisation process. When the spectrum is examined, ν (C-C) at 1530 cm^{-1} shows the aromatic bond vibration. To better show the peaks obtained, the spectra are presented as three specific regions. The band observed at 3650-3215 cm^{-1} is due to ν (N-H). This band can be attributed to the formation of urethane and mainly blocked urea groups, evidenced by the presence of the shoulder observed at 1740 cm^{-1}. On the other hand, FTIR technique was used to show that chitosan and lignin are coordinated. Characteristically, gPU-induced bonds are present with peaks in 1715, 1460, 1423, 1336, 1090 cm^{-1}. Chitosan shows a broad band at 3300 cm^{-1} due to the presence of ν(O-H) groups in its content. The band observed at about 1715 cm^{-1} can be attributed to the carboxylic acid group ν(C=O) [15].



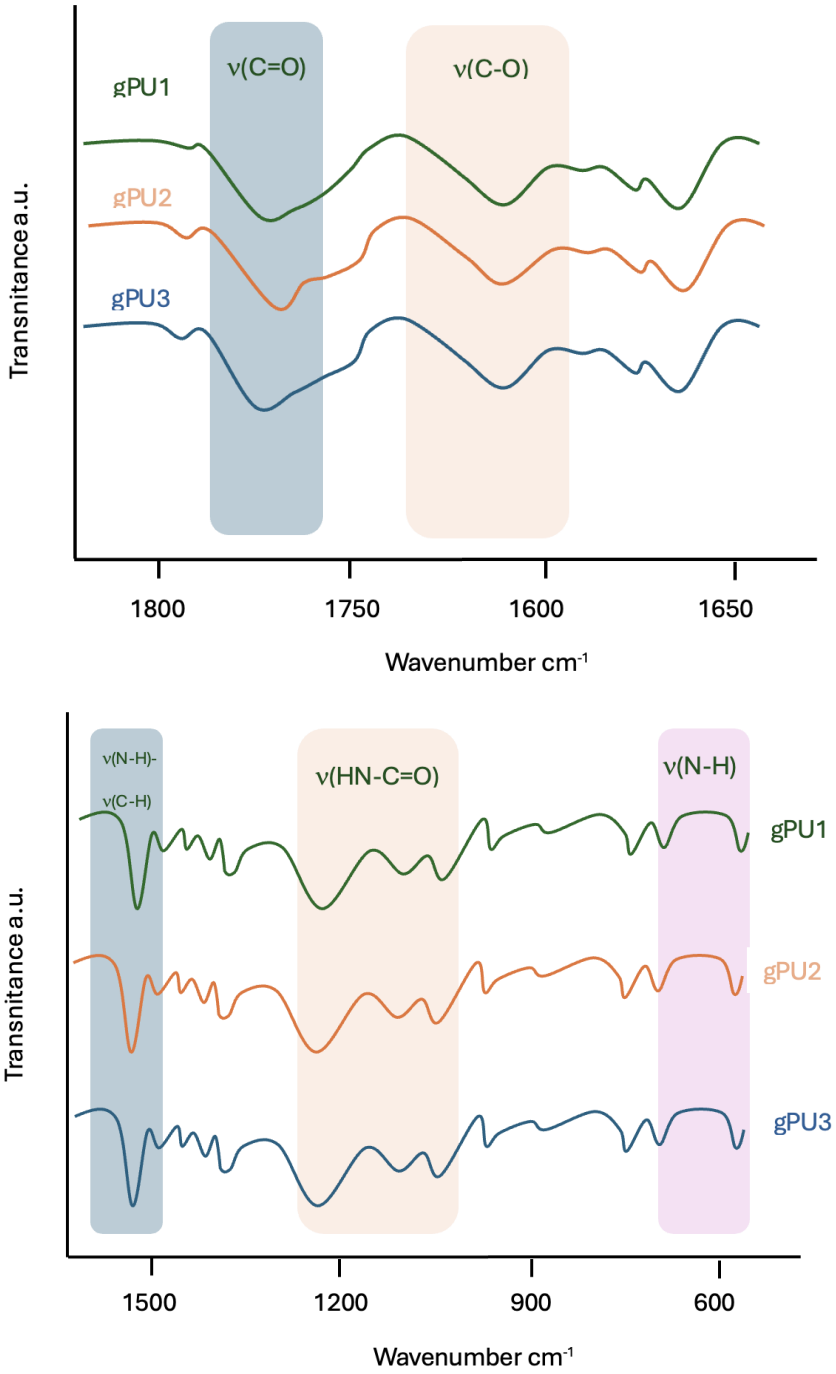


Figure 4: FTIR Spectra of gPU

4. Discussion and Conclusion

In this study, polycondensation of lignin (KL) obtained from waste corn cob and chitosan obtained from shrimp shells was carried out and polyurethane initiators, polyol and isocyanate alternatives were synthesised. One of the important points here is that five carbon diol compound was used as a chain extender in polymerisation. The reaction efficiency was increased by using tinoctoate as a catalyst. It is seen that the reaction conditions play an effective role on the polymerisation yield and degree. Temperature, pressure and gas atmosphere were found to be effective mechanisms during the reaction. Increasing the temperature gradually and increasing the pressure slowly facilitated the water outflow. In order to remove the water molecules released as a result of condensation in an aqueous environment, a rapid distillation process seems to give effective results. Chemical characterisation of lignin (KL) with chitosan proved to synthesise new block polyurethane prepolymers. The chain extender agent was shown to be coordinated to the chain by FTIR test. The results proved that blocked isocyanate groups are applicable for the synthesis of lignin-based polyurethanes. The use of biomass in the preparation of these materials was found to be appropriate. Finally, in the use of the obtained prepolymers in the filter sector, it is thought that their applicability as adhesives can be sealed in harmony with steel substrates.

5. Acknowledge

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