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Synthesis of Polyurethane Solution

(Castor Oil Based Polyol for Polyurethane)

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Abstract

Around 160 million hector unused is available in India. India is the world's largest producer of castor oil, producing over 75% of the total world's supply. There are over a hundred companies in India-small and medium-that are into castor oil production, producing a variety of the basic grades o castor oil. All the above factors make it imperative that the India industry relooks at the castor oil sector in order to devise suitable strategies to derive the most benefits from such an attractive confluence of factors. Castor oil is unique owing to its exceptional diversity of application. The oil and its derivatives are used in over 100 different applications in diverse industries such as paints, lubricants, pharma, cosmetics, paper, rubber and more. Recent developments have successfully derived polyol from natural oils and synthesized range of PU product from them. However, making flexible solution from natural oil polyol is still proving challenging. The goal of this thesis is to understand the potentials and the limitations of natural oil as an alternative to petroleum polyol. An initial attempt to understand natural oil polyol showed that flexible solution could be synthesized from castor oil, which produced a rigid solution. Characterization results indicate that the glass transition temperature (T_g) was the predominant factor that determines the rigidity of the solution. The high T_g of solution was attributed to the low number of covalent bond between cross linkers.

***Keywords**: Polyurethane, castor oil polyol*

I. POLYURETHANE [1]

Polyurethane, commonly abbreviated PU, is any polymer consisting of a chain of organic units joined by urethane links (-NH-(C=O)-O-). Polyurethane polymers are formed by reacting a monomer containing at least two Isocyanates functional groups with another monomer containing at least two alcohol groups in presence of a catalyst.

1.2 Main Raw Materials

a) Polyol
b) Isocyanates
c) Chain Extender and Cross Linker

1.3 Other Additives

a) Catalyst
b) Blowing Agent

2. Natural oil polyol-based Polyurethanes [1, 2]

Natural oil polyol derived from castor have been successfully used in PU elastomers synthesis. Authors reported comparable hardness/modulus between elastomers synthesized from petroleum polyether polyol and natural oil polyol. Thermal degradation experiments indicated that natural oil polyol derived elastomers are superior to petroleum polyol derived samples in both thermal stability and oxidation resistance. Researchers believe that the thermal stability and oxidation resistance are attributable to a high content of hydrocarbons in natural oil polyol as oppose to the alkaline oxide in petroleum polyol. Other than processed natural oil polyol, unprocessed castor oil containing hydroxyls naturally, have also been experimented as a potential polyol for elastomers synthesis. Unlike the processed polyol, the addition of castor oil was shown to lower the Young's modulus and improve elongation properties. Although both castor oil and processed oil polyol are considered as natural oil polyol, their resulting elastomers differ in mechanical properties. Some believe that the difference in heterogeneity between processed polyol and castor oil cause the differences in elastomers properties. When functional hydroxyl groups are added to a triglyceride molecule, depending upon the location of unsaturation sites and process method used, the number of hydroxyls, or functionality, as well as the location of the hydroxyls varies significantly. A naturally occurring polyol, such as castor oil, has less variation in its fatty acid residue structures, for castor oil ~ 90% of the fatty acid residues are ricinoleic acid, Zlanatic etc. Al. surveyed a range of natural oil polyol and their elastomers and concluded mechanical properties are largely dependent upon the cross linking density and functionality of the polyol, and less influenced by the position of the hydroxyls. However when low functionality polyol are used, the heterogeneity of the polyol was shown to have an adverse effect on both young’s modulus and elongation at break. Authors further speculated that the loss in elongation properties, in particular, was due to the imperfections introduced through the heterogeneity of natural oil polyol.

Aside from elastomers applications, rigid solution, which is the second largest family of PU products, can also benefit from using natural oil polyol. Similar to the elastomers cases, rigid solutions made from soybean oil-derived polyol showed superior thermal stability and oxidation resistance to the petroleum polyol solutions. Guo et. al. suggested that the absence of the ether linkage is the key to improved thermal and oxidation properties. Mechanical testing on rigid solutions synthesized from a number of soybean oil-derived polyol showed that these rigid solutions delivered similar compressive properties to the petroleum solutions. Thermal conductivity of all solutions tested showed no significant changes and was independent of polyol properties. Other than soybean oil polyol, rigid solution can also be made from rapeseed oil-derived polyol, however, the authors recommended that both polyol reactivity and long-term stability of the polyol should be further understood.

The most important family of PU products is flexible solutions however, making such solutions from natural oil polyol has found limited success. John and coworkers synthesized flexible solution using entirely soybean oil polyol and concluded that soybean oil polyol can be potentially used. However, the SEM images provided show large amounts of closed cells. Herrington et. al. and Babb et. al., instead of using entirely soybean oil polyol, replaced part of petroleum polyol with soybean oil-derived polyol and found improvements in solution load bearing properties without sacrifices in the number of open cells. Zhang et. al. further studied flexible solutions made with different substituent polyol including a soybean oil-derived polyol and concluded that both changes in hard domain morphology and the addition of a second soft domain with high glass transition temperature increased soybean polyol solution modulus. There has been some success in using castor oil, however, samples made from this natural polyol are limited to low resiliency solutions, which means only partial recovery can be attained immediately after deformation.

The goal of this research is to understand the potentials and the limitations of natural oil polyol and ultimately synthesize flexible solutions using entirely natural oil polyol.

3. Sole as Castor oil polyol for polyurethane [1, 2]

3.1 Overview

In this chapter, were selected as the sole polyol components for polyurethane (PU) flexible solution synthesis. The goal is to examine whether natural oil polyol can be used direct for flexible solution synthesis and to understand the differences between petroleum and natural oil polyol.

The thermal-mechanical study showed that the flexibility of a solution was closely associated with its glass transition temperature (T_g). Further examination of the data suggested that polyol molecular weight could have played a vital role in determining T_g. Although castor oil without modification is not the ideal sole polyol components for flexible solutions, they provided us the first step toward understanding natural oil polyol.

3.2 Introduction

Flexible solution is the single largest product family in PU. The unparallel properties offered by PU, such as vibration damping, sound insulation, impact protection and consumer comfort, have made this material an indispensable component in furnishing, transportation and packaging industries.

In the recent years, the price of crude oil has escalated raising many concerns over the stability and the sustainability of petroleum resources. The rising cost of crude oil also impacts the cost of PU products, because majority of the raw materials, such as polyol and Isocyanates used in flexible solutions, are petroleum derivatives. Finding an alternative feedstock for PU has become highly desirable for both economic and environmental reasons. Natural oils, such as soybean and safflower oils, have been shown to be a potential bio-renewable feedstock for PU.

Early research works has focused on synthesizing elastomers and rigid solutions from entirely natural oil polyol and are proven to be successful; however, challenges remain in making flexible solutions, the most significant PU product, using entirely natural oil polyol. Thus far, castor oil, a naturally occurring polyol, has been used as the sole polyol component for flexible solution synthesis. The samples obtained, although are low resiliency flexible solutions meaning slow recovery from deformation, are the first success case of entirely natural oil polyol-based flexible solutions. On the other hand, polyol derived from natural oils using methods stated. such as SBOP, have not been reported as a successful sole polyol component in flexible solution synthesis. In the open literatures, no mention has been made regarding the reason why these processed natural oil polyol are not used in flexible solution as the sole polyol components.

As the goal of this research is to understand the potentials and the limitations of natural oil polyol and ultimately synthesize flexible solutions entirely from them, understanding both castor oil and SBOP is naturally the first step. Four polyol, two petroleum and two natural oil polyol, were selected and used in polyurethane solutions synthesis.

4. Experiment [3, 5, 7]

4.1 Castor oil polyol properties

Table 4.1 Properties of the castor oil based polyol used

Polyol	Castor oil
OH (mg KOH/g)	163
Molecular weight(g/mol)	930
T_g (°C)	64
ΔC_p (J/g/°C)	0.88

Formulation

Table No. 4.2 Castor based polyol formulation for PU solution

Ingredient	**PHR**
Castor derivative OH-160 gm/mol	100
Distilled water	2.00
Silicone surfactant	0.60
Tertiary amine catalyst	0.08
Di-butyl-tin-di-laurite	2.00
TDI weight (gm, index = 100)	74.5
Solution density (kg/m^3)	34.60

4.2 Solution Synthesis

All samples were made based upon a total mixture weight of 250 g. The amount of TDI used stoichiometrically balanced NCO to active hydrogen species, i.e. Isocyanates index = 100. The amounts of water used were calculated to keep hard segment (HS) contents at ~28% between samples. All ingredients except the TDI were weighed into a 500 mL polypropylene beaker cup and mixed using a 10-in shop drill equipped with a 3-inch diameter mixing blade for 30 seconds at 1500 rpm. At the end of the mixing period, pre-measured TDI was added to the mixing cup and the mixing continued for another 6 seconds.

The contents were quickly transferred into a 170 fl. oz paper bucket.

The mixture was allowed to cure at room temperature for approximately 30 seconds.

Before it was transferred into a pre-heated curing oven controlled at 70 ± 1 °C.

For adiabatic temperature rise measurements during solutioning, the samples were kept in the ambient and discarded after the experiments. Castor oil is a triglyceride fatty acid and approximately 90 % of its fatty acid residues are ricinoleic acid and the rest 10 % varying mainly among oleic, linoleic, steric and palmitic acids.

The f_n of castor oil is 2. Toluene diisocyanate (TDI) used is an 80:20 mixture of 2,4 and 2,6 isomers. Isocyanates in excess of that needed to react with the OH groups on the polyol reacts with distilled water to form CO_2, which acts as the only solution blowing agent. Gelling and blowing catalysts, solution of 33% triethylenediamine and 67% dipropylene glycol, dibutyltindilaurat, and 70 % Bis-(2-

dimethylaminoethyl)ether and 30% dipropylene glycol, solution of 33% triethylenediamine and 67% dipropylene glycol and dibutyltindilaurat are both gelling catalysts used to accelerate the reaction of NCO with OH. A solution of 33 wt% triethylene diamine in dipropylene glycol and was used as the gelling catalyst. A strong gelling reaction catalyst comprised of dibutyltin dilaurate (DBTDL) and was used in solution formulations

A blowing catalyst used to accelerate the reaction of NCO with water, is a solution of 70 wt% bis(2-dimethylaminoethyl)ether in dipropylene glycol. Single surfactant was used in this study to stabilize the solution cellular a structure is a silicone-based, molded solution surfactant.

4.3 Characterization

Adiabatic Temperature Rise

Temperature profiles during solution were taken using type J thermocouples made in-house. Two fine wires of Iron and constantan, 0.25 mm in diameter. The wires were first cut into 30 cm long pieces and the nylon jacket at one end was stripped. The exposed wires, one iron wire and one constantan wire, were brought to form a knot by twisting the exposed ends together by hand. A propane blowtorch was then brought to a quick contact with the twisted ends thus melting the two metals to form a welded tip. The thermocouple is accurate to $\leq 0.1\ ^{o}C$ in measurements. The analogue temperature reading was recorded via an analogue connection on a rheometer at 1 Hz frequency. The conversion of the analogue signals to temperature reading was performed via a pre-measured calibration curve.

4.4 Results and Discussion

During solution, both gelling and blowing reactions are exothermic reactions. As a solution takes on its shape, the cellular structures developed act as a layer of insulation around the centre of a solution bun making it an adiabatic reactor. Figure 2.2 shows the adiabatic temperature rise profiles taken of the solution buns. One of the characteristics of an adiabatic temperature rise is its direct relationship with reaction kinetics. In the case of PU solution formation, the temperature change is related to the consumption of a common reactant in both gelling and blowing reactions, Isocyanates [24]. Equation 2.1 shows the relationship between the Isocyanates conversion and the temperature rise. The calculated Isocyanates conversions from the temperature rises

$$p(NCO) = \frac{r\Delta T_m}{\Delta T_{rxn}}$$

$$\Delta T_{rxn} = \frac{Q}{C_p m_T} = \frac{\Delta H_{r,u}\frac{m_w}{M_w} + \Delta H_{r,r}\frac{m_{OH}}{M_{OH}} f_n}{C_p m_T}$$

Where,

p is the Isocyanates conversion,

r is the stoichiometric ratio of functional groups, which is unity in this case,

ΔT_m is the temperature rise during foaming measured via thermocouple,

ΔT_{rxn} is the maximum temperature rise based on an adiabatic reactor,

Q is the total amount of heat generated in the unit of J,

ΔH_r is the heat of reaction in the unit of J/g, m is reactant mass,

C_p is the specific heat capacity of solution, which is 1.81 $J/g/^{o}C$,

M is the molecular weight in the unit of g/mol, f_n is polyol functionality,

and the subscripts, u,r, w, OH, and T indicate urea, urethane, water, polyol and total, respectively.

The heats of reaction for urea and urethane formation were taken as –125.5 kJ/mol and –93.9 kJ/mol].

The Isocyanates conversion versus time curves for all four solution samples are very similar. This similarity required changes in the gelling catalyst.

Furthermore, the solutions collapsed during the curing step. The gelling reaction, when catalyzed by

Test trials on the effect of gelling catalyst were performed at room temperature by reacting a polyol with TDI only and monitoring the reaction using a rheometer. Castor oil

. During the first 20 seconds of reaction, TDI was consumed at a 10 % faster in castor oil

The difference in TDI consumption could be attributed to the difference in urethane formation rates.

The final conversions of isocyanate, based on the temperature profiles shown, are ~80% in all solutions at t = 100 seconds. The reason isocyanate conversion did not reach the theoretical 100% conversion is likely due to vitrification of the hard segments, which makes the foaming mixture inhomogeneous.

5. CONCLUSIONS

In this study, we synthesized PU solutions from polyol. It was found that castor oil solutions have T_g's around 5 ºC. The differences in solution T_g's were attributed the differences in crosslinking densities of their soft segments. Although castor oil is not ideal for flexible solution formulations, the result did identify that the T_g of solution is the key parameter in determining the flexibility of PU solutions. Therefore, our future investigations will aim to find ways to lower the T_g of a PU through natural oil polyol designs.

Mechanical property of the solutions also varied as indicated by the DMA study. The plateau modulus is the highest for solution synthesized using the high molecular weight petroleum polyol and the lowest for the solution synthesized using the low molecular weight petroleum polyol. The volume fraction of phase-separated hard domains plays an essential role in determining mechanical properties and is believed to be dependent upon polyol used through its influence on the segmental length of polyurethane.

The route, aimed to find ways to lower the T_g of a PU and thus making natural oil polyol a potential candidate as the sole polyol component in flexible solutions. A series of model polyol based on natural oils were synthesized and studied to establish a structure-property relationship for natural oil polyol-based PUs.

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