A novel one shot synthesis and characterization for castor oil based polyurethane foam

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ABSTRACT

Polyurethane foam (PU) was prepared from pre-polymer of toluene diisocyanate (TDI); and castor oil (C.O.) with dibutyl tin dilaurate (DBTDL) catalyst. Water was used as blowing agent. The rate of forming was increased by increasing catalyst and water content. On other hand the cell size of the PU decreased with increasing amount of the catalyst and water content. Castor oil is obtained from natural source and easily available, it is harmless polyl compare to other polyol’s used for preparing PU. In the present work, different parameters such as effect of OH to NCO ratio, effect of catalyst and effect of blowing agent was optimized. PU was characterized by Fourier Transform Infrared Spectroscopy (FTIR). The thermal behavior of PU was studied by Differential Scanning calorimeter (DSC).

Keywords: Castor oil; Toluene diisocyanate; Polyurethane foam; FTIR.

1. INTRODUCTION

The invention of polyurethane was done by Otto Bayer and his coworkers at the laboratories of I.G. Farben in Leverkusen, Germany in the 1937. Polyurethane foam has been commercially used in variety of applications. The foams surrounds us in today’s society, playing an important role in many industries and our daily lives. Polyurethane foam is found everywhere in our modern world, it is used as thermal insulating materials for construction, for insulation in electric appliances viz. refrigerators and freezers; used in disposable packaging for food, in the cushioning, in civil engineering and geotechnical applications. Polyurethane foam consists of a solid polymer matrix and a gaseous phase formed by blowing agents. Foaming of polymeric materials is carried out by mechanical, chemical or physical means. The most widely used method involves dispersing a gas throughout a fluid polymer phase and stabilizing the resultant foam. In most systems, foams are allowed to expand before stabilizing the system. It is basically produced using various raw materials such as polyol, isocyanate, water, catalyst and surfactant. Among all, polyol and isocyanate are mixed to form polyurethane linkage. Other components such as: water is added as blowing agent for foam foaming; Catalyst and surfactant are function as promoting nucleation as well as stabilizing the foam formation during foam development stage [1,2].
In the beginning, aliphatic diisocyanate and diamine forming polyurea was focused, later diamine was replaced by glycol to obtain polyurethane. The glycol based polyurethane gives the interesting properties. Polyisocyanates became commercially available in the year 1952, soon after the commercial scale production of polyurethane was witnessed (after World War II) from toluene diisocyanate and polyester polyols. In the years of 1952-1954, different polyester-polyisocyanate systems were developed by Bayer [3].

The chemistry, application techniques and material properties of polyurethane were developed and improved [4]. As polyurethane is light in weight, good insulation quality, quick reaction time and high expansion rate; polyurethane is also used as sealants and in asphalt modification for the road construction. The polyurethane is used to raise sunken concrete roadway, to improve the performance and to increase load bearing capacity [5].

Polyurethane has become such largely used because of its varieties of properties such as excellent light weight, strength to weight ratio performance, it offer degree of comfort, protection and utility not matched by other material. Three different types of polyurethane were available on the basis of its cell structure, i.e. Flexible, semi-flexible and rigid. Flexible foam is found on having open-cells cellular structure. Rigid foam having closed-cells cellular structure while semi-flexible having both types of cells [6].

Different polyol may be used for the production of foam but sometime it proves costly and may hazardous while handling. To promote the eco friendly environment, castor oil was used as one of the component as polyol for polyurethane manufacturing [7]. Castor oil is natural oil which is cheap and easy to handling with zero hazardous effect. Thus, in order to minimize the environmental problems, an alternative polyol is used for polyurethane manufacturing [8].

In the present work, castor oil was used with toluene diisocyanate to form castor oil based polyurethane foam. Different foam was obtained with different OH to NCO ratio. Reaction parameters was optimized such as effect of catalyst, effect of molar ratio, effect of blowing agent and effect of density. Polyurethane foam was characterized by FTIR-ATR (Fourier transform infrared spectroscopy-Attenuated total reflectance) and DSC (Differential scanning calorimeter).

2. MATERIALS AND METHODOLOGY

2.1 Materials

Castor oil was taken from raw material storage, RCPL, Patan. Dibutyl tin dilaurate was purchased from Ultima chemicals, Mumbai. Toluene diisocyanate (TDI) and xylene were purchased from Merck.
India Private Ltd. Solvents and other chemicals were used of A.R grade and used after routine purification.

2.2 Methodology

2.2.1 Synthesis of polyurethane pre-polymer

Polyurethane pre-polymer (PUP) was prepared by using castor oil and toluene diisocyanate (TDI). Raw materials were added into the four neck round bottom flask which was equipped with motor stirrer and heating source. Pre-polymerization was carried out at 80°C temperature under nitrogen atmosphere for 1hour reaction time.

2.2.2 Synthesis of polyurethane foam

The polyurethane foam was prepared by one shot method. Different volume of castor oil was taken into a beaker, add R.O. water as blowing agent and stir well for while. Then add DBTDL as catalyst, again stir well. After proper mixing, PUP was added into above prepared polyol mixture. Motor stirrer was used for stirring the mixture for 30seconds at 500rpm. Creamy mixture was formed; pour the mixture into mold where foam was cured for 2-4hours at room temperature. Various PU was prepared with different OH to NCO ratio.

2.2.3 Hardness determination

The determination of hardness of polyurethane foam was carried out using penetrometer shown in figure: 1.
2.2.4 Density determination

Density of polyurethane was measured according to ASTM D1622. The size of the specimen was 30 x 30 x 30mm. Densities of five specimens were measured and averaged for each sample.

2.2.5 FTIR spectroscopy

The FTIR spectroscopy of PU was done using Attenuated total reflectance (ATR) technique.

2.2.6 DSC of PU

Thermal behavior of PU was studied using differential scanning calorimeter. The sample was run from 250°C to 350°C temperature. Nitrogen was used as inert purge gas.

3. RESULT AND DISCUSSION

3.1 Effect of catalysts

Table: 1 It shows the effect of catalyst amount on foam density

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Raw materials</th>
<th>Catalyst (gm)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C.O., PUP</td>
<td>0.2</td>
<td>108.2</td>
</tr>
<tr>
<td>2</td>
<td>C.O., PUP</td>
<td>0.3</td>
<td>114.5</td>
</tr>
<tr>
<td>3</td>
<td>C.O., PUP</td>
<td>0.4</td>
<td>118.8</td>
</tr>
</tbody>
</table>

The effect of catalyst amount was shown in table: 1. The rate of forming foam was assessed from the inverse of the characteristic times such as the cream time, gel time, and tack free time. The cream time is defined as the time when the color of mixed reactants becomes brightened. The gel time is the time when the stable spatial shape is formed. The tack free time is the time when the product can be detached from the mold. The rate of forming the foam increases with the increase of the content of the catalyst. In addition, the catalyst promotes the faster cream time and the gel time. The cell size of the PUF decreases with the increase of the catalyst.
3.2 Effect of blowing agents

Table: 2 It shows the effect of blowing agent amount on foam density

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Raw materials</th>
<th>Blowing agent (ml)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C.O., PUP</td>
<td>1</td>
<td>108.2</td>
</tr>
<tr>
<td>2</td>
<td>C.O., PUP</td>
<td>2</td>
<td>114.5</td>
</tr>
<tr>
<td>3</td>
<td>C.O., PUP</td>
<td>3</td>
<td>118.8</td>
</tr>
</tbody>
</table>

The effect of water as blowing agent was shown in table: 2. The rate of forming foam increases with the increase in water content. This was, because of probably increase in the temperature of the reactants by the heat of reaction evolved by the reaction between water and isocyanate. The effect of the blowing catalyst content on the density is shown. It was observed that the density of the polyurethane foam using water as the blowing agent increase with the blowing catalyst content.

3.3 Effect of OH and NCO ratio

Table: 3 It shows the effect of OH and NCO ratio on foam type

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Raw materials</th>
<th>OH to NCO Ratio</th>
<th>Density (kg/m³)</th>
<th>Type of foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C.O., PUP</td>
<td>1:0.75</td>
<td>108.2</td>
<td>Flexible</td>
</tr>
<tr>
<td>2</td>
<td>C.O., PUP</td>
<td>1:0.75</td>
<td>114.5</td>
<td>Flexible</td>
</tr>
<tr>
<td>3</td>
<td>C.O., PUP</td>
<td>1:0.75</td>
<td>118.8</td>
<td>Flexible</td>
</tr>
<tr>
<td>4</td>
<td>C.O., PUP</td>
<td>1:1</td>
<td>133.0</td>
<td>Semi-flexible</td>
</tr>
<tr>
<td>5</td>
<td>C.O., PUP</td>
<td>1:1</td>
<td>142.5</td>
<td>Semi-flexible</td>
</tr>
<tr>
<td>6</td>
<td>C.O., PUP</td>
<td>1:1</td>
<td>147.1</td>
<td>Semi-flexible</td>
</tr>
<tr>
<td>7</td>
<td>C.O., PUP</td>
<td>1:1.25</td>
<td>175.6</td>
<td>Rigid</td>
</tr>
<tr>
<td>8</td>
<td>C.O., PUP</td>
<td>1:1.25</td>
<td>177.0</td>
<td>Rigid</td>
</tr>
<tr>
<td>9</td>
<td>C.O., PUP</td>
<td>1:1.25</td>
<td>183.8</td>
<td>Rigid</td>
</tr>
</tbody>
</table>

The effect of OH and NCO ratio was shown in table: 3. Different ratio of OH to NCO was studied such as 1:0.75, 1:1 and 1:1.25. In case of 1:0.75 ratio, open cell flexible foam was produced where no closed cell was observed. Semi-flexible was observed in case of 1:1 ratio where both open and closed cell was observed. While 1:1.25 ratio results into the rigid foam.
3.4 Effect of density

Effect of density of PU foam was optimized and the results were tabulated in table: 2. Density is a most important parameter to control the mechanical and thermal properties of closed cell and open cell foams. Density of PU foam was found higher when blowing agent was increased.

3.5 FTIR spectroscopy

The FTIR of PU was shown in figure: 1. The structure of PU contains N-H, -CH₂, C=O, C-N and C-O-C linkages. The medium vibration was observed at 3304.53 cm⁻¹ due to N-H functional group. The strong band was observed 2853.94 cm⁻¹ which indicates the presence of -CH₂ streching frequency. C=O streching frequency was observed at 1728.08 cm⁻¹. The bending frequency was observed at 1531.03 cm⁻¹ due to C-N group. The bending C-O-C frequency was observed at 1057.11 cm⁻¹. Above FTIR spectrum confirms the PU structure.

![FTIR spectrum of PU](image)

**Figure: 1**
3.6 DSC of PU

The DSC curve of polyurethane foam was shown in figure: 2. There was no significance changes occurred till 205°C, as the prepared PU may be thermally stable up to that temperature. Beyond 205°C, sample degradation may start.

4. CONCLUSION

Polyurethane foam is thermoplastic and thermoset in nature. Various polyol can be utilized as one of raw materials to produce polyurethane foam. Castor oil is among that, but as the long chain length imparts the good foaming properties. Castor oil was cheap, non-hazardous and easily available in market. All types of foam such as, flexible, semi-flexible and rigid can be prepared with comparatively low density value.

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REFRENCES


