A Review on Castor Oil based Polyurethane Adhesive

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Abstract: The use of raw materials from renewable sources to synthesis polyurethane adhesive is important from social, environmental and economic view as compared to those produced form petrochemical sources. Polyurethanes based on castor oil were synthesized with polyols and toluene diisocyanate, and amine as a catalyst. The degree of swelling, mechanical properties, and polymerization kinetics was greatly affected by the diisocyanate nature. The aim of this review paper is to give a fundamental description of castor oil and various application of polyurethane adhesive like wood, metal, etc.

Keywords: Adhesive, polyols, Castor oil, Isocyanate, Polyurethane.

1. INTRODUCTION

Adhesive are used from long time. The scientist Otto Bayer first invented polyurethanes in 1940.[2] There are various natural adhesive available such as fish glue, animal glue, casein glue, etc. The intermolecular forces between the adhesive and the substrate help to improve the strength and serviceability. Different polymers have been used as adhesives like silicon, polyacrylates, and rubber, but polyurethanes are the most widely in use adhesive due to various properties like their chemistry versatility, good adhesion properties, resistance to weathering, and formulation flexibility.[1] They effectively wet the surface and form bond to textile fibers, metals, plastics, wood, ceramics, rubber, and leather.[3] Polyurethanes based adhesive used by a wide range of application like transport, building, packing, goods and furniture industries.[1]

Polyurethane adhesive are usually produced by reacting (petroleum based) polyols with diisocyanates. Since the beginning of the 21st century, the increasing concern over environmental pollution has forced the industry to develop environmentally friendly adhesive. Which gives renewability; biodegradability.[3] Solventless adhesive from renewable sources are greatly appreciated by the research since they can be produced at low prices and can be biodegradable.[1]

Castor oil, a triglyceride of ricinoleic, is a naturally occurring and suitable monomer for polyurethane production, whose viscosity depends on the chain length and unsaturation degree of the fatty acid. The –NCO groups of the diisocyanate compound react with the –OH group of the castor oil, which become part of the network and will therefore not vaporize out of the adhesive as a solvent.[1] Castor oil is a vegetable oil obtained by pressing the seeds of the castor oil plant (Ricinus communis).

Fig.1 The structure of castor oil[13]
Table 1: Composition of castor oil [13]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Acid Name</th>
<th>Average % range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ricinoleic acid</td>
<td>95 to 85 %</td>
</tr>
<tr>
<td>2</td>
<td>Oleic acid</td>
<td>6 to 2%</td>
</tr>
<tr>
<td>3</td>
<td>Linoleic acid</td>
<td>5 to 1%</td>
</tr>
<tr>
<td>4</td>
<td>Linolenic acid</td>
<td>1 to 0.5 %</td>
</tr>
<tr>
<td>5</td>
<td>Stearic acid</td>
<td>1 to 0.5 %</td>
</tr>
<tr>
<td>6</td>
<td>Palmitic acid</td>
<td>1 to 0.5 %</td>
</tr>
<tr>
<td>7</td>
<td>Dihydroxystearic acid</td>
<td>0.5 to 0.3 %</td>
</tr>
<tr>
<td>8</td>
<td>Other</td>
<td>0.5 to 0.2 %</td>
</tr>
</tbody>
</table>

Table 2: Characterization of castor oil [13]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acid Index (mg/KOH/g) max</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Gardner colour-max</td>
<td>Pale Yellow</td>
</tr>
<tr>
<td>3</td>
<td>Hydroxyl Index (mg/KOH/g)</td>
<td>160-170</td>
</tr>
<tr>
<td>4</td>
<td>Specific Gravity</td>
<td>0.954-0.967</td>
</tr>
<tr>
<td>5</td>
<td>Index of Reflection 25°c</td>
<td>1.4764-1.4778</td>
</tr>
<tr>
<td>6</td>
<td>Saponification index</td>
<td>176-178</td>
</tr>
<tr>
<td>7</td>
<td>Moisture &amp; Volatility</td>
<td>0.5% max.</td>
</tr>
<tr>
<td>8</td>
<td>Boiling Point</td>
<td>313 °C</td>
</tr>
<tr>
<td>9</td>
<td>Melting Point</td>
<td>5 °C</td>
</tr>
<tr>
<td>10</td>
<td>Molecular Weight</td>
<td>248</td>
</tr>
</tbody>
</table>

India is the leading producer and exporter of castor oil in the world, followed by China and Brazil. The states of Gujarat & Rajasthan contribute 90% of the total castor produced in India. The major importers of castor oil in the world market are European Union, US and Japan. The world demand for castor oil is estimated to grow at the rate of 5 to 7% per annum.[6] The present demand for the castor oil product is estimated at 1,250 tonnes per annum. The demand is expected to reach at 2,947 tonnes by the year 2017.[6]

Polyurethane polymers are traditionally and most commonly formed by reacting a di- or polyisocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule.[8,10]

1.1 ISOCYANATES

Isocyanates are very reactive materials which makes them useful in making polymers. The diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI), aromatic isocyanates are more reactive than aliphatic isocyanates, such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI). Most of the isocyanates are difunctional that is they have exactly two isocyanate groups per molecule.[8,12]

Properties of Isocyanate:[8,12]

1.1.1 Toluene di-isocyanate (TDI):
- Aromatic
- React faster with hydroxyl containing compound than aliphatic isocyanates
- Good stability to U.V. light
- Cyanate group present 48%
1.1.2 Diphynylmethane di-isocyanate (MDI):
- Extremely durable
- Toughness
- Stable to U.V. exposure
- Cyanate group present 3-30%

1.1.3 Hexamethylene di-isocynate (HDI):
- Aliphatic
- React slower with hydroxyl containing compound than aromatic
- Reasonable than aromatic
- Reasonable curing time
- It is used mostly coating purpose
- Flexible coating obtained
- Cyanate group present 3-30%

1.2 POLYOLS

Polyols are polymers in their own right and have on average two or more hydroxyl groups per molecule. Naturally occurring polyols are:

1.2.1 Polyether polyols

Polyether polyols are mostly made by co-polymerizing ethylene oxide and propylene oxide with a suitable polyol precursor. Eg. Glycerol, Adipic acid, Diethylene glycol.[10]

Properties of Polyether polyols [8,12]
- Polyether polyols molecular weight required (1000-4000) are commonly used in coating
- Softer
- More flexible
- More resistance to hydrolysis
- Resistance to oxidative degradation

1.2.2 Polyester polyols

Polyester polyols are made similarly to polyester polymers. Eg. Ethylene oxide (PEOX), Propylene oxide (PPOX).[10]

Properties of Polyester polyols [8,12]
- Linear and branch polyester polyols molecular weight required (500-5000)
- It is used for adhesive
- Low cost

1.3 ADHESIVE

An adhesive is material which brings two surfaces together.[10] Following are the Types of adhesive[11,12]

1.3.1 Types by origin

1.3.1 Natural adhesives
1.3.2 Semi synthetic adhesive
1.3.3 Synthetic adhesives
1.3.2 Types by reactivity

1.3.2.1 Reactive adhesives
   1.3.2.1.1 Multi-part adhesives
   1.3.2.1.2 One-part adhesives

1.3.2.2 Non-reactive adhesives
   1.3.2.2.1 Drying adhesives
   1.3.2.2.2 Pressure-sensitive adhesives
   1.3.2.2.3 Contact adhesives
   1.3.2.2.4 Hot adhesives

2. LITERATURE REVIEW

Bianca et.al., worked on A Solventless Castor Oil based PU adhesive for wood and foam substrates they were prepared the solventless castor oil-based PU adhesives were prepared with NCO/OH molar ratios of 1, 2, or 3 having dibutyltin dilaurate (DBTL) and triethylenediamine (TEDA) as catalysts. The tack-free time of the solventless PU adhesives was dependent on the catalyst concentration. The NCO/OH molar ratio influence the mechanical properties. The solventless PU adhesive foam joints showed peeling strength values 75% higher than that of a solvent-based commercial adhesive. The solventless PU adhesive wood joints showed lap shear strength values 20% higher than that of a commercialized solvent-based adhesive used for wood.[1]

Keyur et.al., worked on Castor oil based polyurethane adhesive for wood-wood bonding and they found that most adhesives are polymeric adhesives and if made from renewable sources they will have low cost and biodegradability which are of importance.[14]

Patel et.al., worked on the Biomaterial Based Novel Polyurethane Adhesive for Wood to Wood and Metal to Metal Bonding and they found that modification on active sites of castor oil to utilize double bond of unsaturated fatty acid and carboxyl group yields new modified or activated polyols, which can be utilized for polyurethane adhesive formulation. The NCO/OH ratio (1.5) was optimized for adhesives as the higher NCO/OH ratio (2.0) increasing cross-linking density and decreases adhesion. Lower NCO/OH ratio (1.0) provides slow cross-linking density and low strength of adhesives.[15]

3. RAW MATERIAL AND METHODOLOGY

The raw materials used for the preparation of castor oil based polyurethane are castor oil which is obtained from the local market, Toluene Di-Isocyanate, Polypropylene Glycol are used as a reactant and amine is used as a catalyst also other additives such as Silicon Oil or Soap solution is used as a surfactant.

Castor oil based polyurethane is synthesizes by the reaction between polyol and an excess of isocynate. The syntheses were performed in a three necks round bottom flask with electrically operated stirrer for mixing of components. In one neck condenser is fitted while through side neck the rod of temperature indicator is dip in the solvent and middle neck is used for mechanical stirrer. The molar ratio of chemicals NCO/OH is [1:1] to [1.5:1] for adhesive. Increase in NCO in formulation is increasing the adhesive property.

The reaction is carried out about 40°C to 50°C for one hour with continuous stirring. The reaction is carried out under condensation polymerization. After polymerization viscosity builds up and eventual gelations take place. This viscous solution is directly use as adhesive.
4. PRODUCT CHARACTERIZATION

Adhesion test has been carried out for determination of adhesion resistance. Tensile strength can be carried out by applying maximum tensile load per unit area expressed in pounds per sq. inch on a tensile testing machine. The cleavage test is conducted by introducing a prying force at one end of a bonded specimen to split the bond apart. The deformation of dimensional change occurring in an adhesive bonded specimen under stress over a period of time is referred as creep and the peel test involves the stripping of a flexible member of an assembly that has been bonded with an adhesive to another member that may be flexible or rigid and express in pound per square inch of width.

Infrared spectroscopy is a technique for identification of compounds, determination of functional groups in organic materials. The gel and surface drying time measured for different NCO/OH ratio. Thermal degradation determined by Thermo-gravimetric analysis. The glass transition temperature of a polymer network is affected by the cross-linking density as well as the chemical structure; increased aromatic content should result in higher Tg where as reduced cross-linking density would have the opposite effect.

The resistance of adhesives to chemical reagents may be determined by exposing bonded specimen to chemical environment.

5. CONCLUSION

In the beginning of the 21st century, the increasing concern over environmental pollution has forced the industry to develop environmentally friendly adhesive. Castor oil based polyurethane adhesive from renewable sources are greatly appreciated by the research since they can be produced at low prices and can be biodegradable, as compared to those produced from petrochemical sources. By use of this method biodegradable castor oil based polyurethane adhesive made.

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