Synthesis and physico-chemical study of polyester polyol of epoxy resin of 1, 1’-bis (3-methyl-4-hydroxy phenyl) cyclohexane and ricinoleic acid and its polyurethanes with polyethylene glycol

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Cardo polyester polyol (acid value, 2.14; hydroxyl value, 91.1 mg KOH/g) has been synthesized by reacting epoxy resin of 1,1’-bis (3-methyl-4-hydroxy phenyl) cyclohexane (EE = 436) and ricinoleic acid (8.94 g) by using triethyl amine (0.5 g) as a catalyst and 1,4-dioxane as a solvent at reflux temperature for 6h. Cardo polyester polyol-TDI based copolyurethanes have been synthesized by reacting polyol (3.0 g) and TDI (0.9 g) in MEK at room temperature by using 20% and 30% PEG-400 on the basis of polyol weight. PU-20 and PU-30 films were cast by controlled evaporation of MEK. The formation of polyol and copolyurethanes are supported by FTIR spectral data. Densities of PU-20 (1.2379 g/cm$^3$) and PU-30 (1.2016 g/cm$^3$) are determined by floatation method at room temperature by using CCl$_4$- n- hexane system. Density decreased with PEG-400 concentration due to increase in intrinsic volume of the repeating unit. Tensile strength, electric strength and volume resistivity of both copolyurethanes decreased with increasing concentration of PEG-400 due to presence of soft and hard segments in polymer chain. PU-20 and PU-30 remained unaffected in pure water and 10% NaCl solution and showed moisture uptake tendency in acidic and alkaline atmosphere. Max. moisture uptake, observed within 24-48h, is 4.7-15% in 10% each of HCl, H$_2$SO$_4$ and HNO$_3$ and 8.7-14.2 % in 10% each of NaOH and KOH solutions. PU-30 has much low water absorption tendency as compared to PU-20 due to increasing PEG-400 concentration. PU-20 and PU-30 remained unaffected in pure water and 10% NaCl solution and showed moisture uptake tendency in acidic and alkaline atmosphere. Max. moisture uptake, observed within 24-48h, is 4.7-15% in 10% each of HCl, H$_2$SO$_4$ and HNO$_3$ and 8.7-14.2 % in 10% each of NaOH and KOH solutions. PU-30 has much low water absorption tendency as compared to PU-20 due to increasing PEG-400 concentration. PU-20 and PU-30 are thermally stable up to about 190-198°C and involved three-step degradation kinetics. No effect of PEG-400 was observed on thermal properties of co polyurethanes. For PU-20, $T_{\text{on}}, T_{\text{on}}$ and $T_{\text{on}}$ are 190, 225.1 and 362.6°C, while for PU-30 they are 198, 235.5 and 369.0°C, respectively. The decomposition ranges are 190-304, 342-440,472-540 and 198-307, 350-430, and 448-590°C, respectively for PU-20 and PU-30. The excellent hydrolytic stability and fairly good thermo-mechanical and electrical properties of PU-20 and PU-30 signify their industrial importance as coating and adhesive materials.

Keywords: Cardo polyester polyol, Chemical resistance, Copolyurethane, Density, Electrical properties, Mechanical properties, Thermal analysis

Introduction
Polyurethanes (PUs) are becoming increasingly important as engineering materials because of their excellent adhesion and abrasion resistance, high cohesive strength, amenable curing speed and properties of both elastomers and plastics$^{1-4}$. PUs effectively wet and readily form H-bonds with textile fibers, metals, plastics, wood, glass, etc. PUs are a very appealing class of polymers for use in the biomedical field because of relatively good biocompatibility, physical properties and the ease with which their properties can be tailored to end use$^{5-9}$. Extent of cross linking, nature of polyol and diisocyanate and curing conditions affect properties of PUs$^{10,11}$. Hydrolytic stability of PUs depends on polyester chain length and type of diisocyanates$^{12}$. Epoxy resins with outstanding physico-chemical properties$^{13}$ are the most useful resins but brittleness with low elongation restricts their use for high performance applications$^{14}$. Epoxy resins have been modified with dienes$^{15}$, acrylates$^{16}$, etc to improve mechanical properties. Highly reactive epoxy ring can also undergo ring opening reaction in presence of acids$^{17}$ to yield polyester polyol (PEP) containing a free hydroxyl group that can be utilized to produce PUs. For economic production of PUs, efforts have been made to prepare PEPs from low cost natural oils and their derivatives$^{18-20}$. Carboxyl groups of ricinoleic and oleic acids of castor oil can be utilized for ring opening reaction. Good compatibility of castor oil with polyethylene glycol (PEG) in all proportions can blend PEG effectively with castor oil or its derivatives to produce PUs.
Hybrid coating materials resulting from inter cross linking network (ICN) mechanism enhance thermal stability, hydrophobicity and impact behaviors as compared to that of blending technique\textsuperscript{21,22}. Epoxy oligomers and diisocyanates based PUs coating systems have attracted the attention of material scientists due to their superior applications as coating, adhesives, filling compounds of high heat resistance and chemical stability against various aggressive agents.

Paper presents synthesis and physico-chemical study of PEP (I) of epoxy resin of 1,1'-bis (3-methyl-4-hydroxy phenyl) cyclohexane (MeBC) and ricinoleic acid and its PUs with PEG.

**Materials and Methods**

**Materials**

Solvents and chemicals were of laboratory grade and purified prior to their use\textsuperscript{23}. MeBC and its epoxy resin were synthesized\textsuperscript{24}. Epoxy equivalent of resin used for PEP synthesis was 436. Toluene diisocyanate (2,4-TDI:2, 6-TDI=80:20) (Narmada Chematur Petrochemicals Ltd., Bharuch), PEG (PEG-400) (S.D.Fine Chemicals, Baroda), ricinoleic acid (Pasand Speciality Chemicals, Rajkot) and triethyl amine catalyst (Spectrochem, Baroda) were used.

**Synthesis of Cardo Polyester Polyol**

A three neck flask (500 ml), equipped with a mechanical stirrer, condenser and thermometer, was placed in water bath and a 0.015 \textit{M} epoxy resin of MeBC (15.2 g) in 1,4-dioxane (30 ml), 0.03 \textit{M} ricinoleic acid (8.94 g) and triethyl amine (0.5 g) were placed and stirred well at room temperature for 5 min. The reaction mixture was refluxed for 6 h with stirring. Excess solvent was distilled off and reddish brown transparent resin was transferred to airtight bottle. Acid value (2.14 mg KOH/g) and hydroxyl value (91 \pm 1.0 mg KOH/g) of the resultant cardo PEP (Fig. 1) were determined using 0.1 \textit{N} ethanolic potassium hydroxide and 1 \textit{N} NaOH, respectively\textsuperscript{25}. Phenolphthalein was used as an indicator. For acid value, resin was dissolved in acetone, while for hydroxyl value acetic anhydride-pyridine (1:3 v/v) mixture was used.

**Synthesis of Cardo Polyester Polyol-TDI based Polyurethane**

To a 100 ml beaker containing 0.002 \textit{M} cardo PEP (3.0 g) in methyl ethyl ketone (MEK, 10 ml) was added 0.005 \textit{M} toluene 2, 4-diisocyanate (TDI, 0.9 g)) in MEK (5 ml) at room temperature and stirred manually for 10 min. The resultant PU solution was poured into a leveled 15 cm x 15 cm glass mold. The solvent was allowed to evaporate with controlled rate. After 24 h, a hard and brittle PU film was removed from the mold (Fig. 2).

**Synthesis of Cardo Copolyurethanes**

To improve flexibility of PU, different proportions of PEG-400 were used. Pre polyurethane
Fig. 2 — Structure of (a) Polyurethane (PU) and (b) Copolyurethane
was synthesized as above and to this 20% (0.6 g) or 30% (0.9 g) PEG-400 (based on PEP) in 5 ml MEK was added drop wise and the reaction mixture was stirred for 10 min. Copolyurethane (CPU) solution was poured into a leveled 15 cm x 15 cm glass mold and the solvent was allowed to evaporate with a controlled rate. Hereafter, CPUs are designated as PU-20 and PU-30 respectively for 20% and 30% PEG-400 in CPU. When PEG-400 content exceeds 30%, the resultant CPU films found to be brittle (Fig. 2).

Measurements
IR (KBr pellet) spectra of PEP and PUs were scanned on a Shimadzu FTIR-8400 spectrometer. Densities of PU-20 (Thickness, 31.7 μm) and PU-30 (Thickness, 31.7 μm) films were determined by floatation method by using CCl$_4$-n-hexane system at room temperature accurate to ±0.0001 g cm$^{-3}$. In six different wide mouth stoppered test tubes, a small piece of film and about 5 ml CCl$_4$ were placed and n-hexane was added drop wise with shaking till the film remained suspended throughout and allowed to equilibrate at room temperature for 24 h. Chemical resistance of the films against water and 10% each of acids, alkalis and salt was carried out by change in weight method at room temperature. Tensile strength (IS: 11298-Pt 2-1987), electric strength (ASTM-D149-92) and volume resistivity (ASTM-D257-92) measurements were done respectively on a Universal Tensile Testing Machine Model No. 1185 at a speed of 50 mm/min., a high voltage tester (Automatic Electric Mumbai) in air at 27°C by using 25/75 mm brass electrodes and Hewlett Packard high resistance meter at 500 V DC after charging for 60 sec. TG thermograms of CPUs were scanned on a Perkin Elmer TGA Model No Pyris-1 at heating rate of 10°C/min in an N$_2$ atmosphere.

Results and Discussion
IR Spectral Analysis
IR spectrum of PEP showed disappearance of peak at 920 cm$^{-1}$ due to terminal epoxy group and appearance of new peaks at 1732.9 cm$^{-1}$ and 3423.9 cm$^{-1}$ due to ester and secondary hydroxyl groups, respectively confirmed formation of cardo PEP (Table 1, Fig. 3). IR spectra (Fig. 3) of PU-20 and PU-30 showed peaks at 3288.4-3423.9 cm$^{-1}$ and 1726.2-1732.9 cm$^{-1}$ due to urethane NH and C=O stretching. Traces of unreacted isocyanate groups may react with moisture in the environment and ultimately converted into amino groups. Presence of unreacted isocyanate and hence amino groups may affect ultimate physico-chemical properties of PUs. Thus, IR spectra confirmed formation of CPUs.

Densities of PU-20 and PU-30
Densities observed are: PU-20, 1.2379±0.0006; and PU-30 1.2016 ± 0.0006 g/cm$^3$. Physical properties of PUs largely depend on chain length and content of soft and hard segments$^{28}$. Decrease in density is mainly observed due to increasing amount of soft segment PEG-400, which causes increase in intrinsic volume of repeat unit in the CPU network.

Mechanical and Electrical Properties of PU-20 and PU-30
Tensile strength (TS), electric strength (ES) and volume resistivity (VR) of PU-20 and PU-30 (Table 2) decreased with increase in PEG-400 content in CPU. Generally, introduction of soft segments including ester and ether groups increases elongation and decreases TS$^{26}$. Increasing amount of hard segment usually results in increase in intermolecular attraction and hence increase in TS$^{26}$. Decrease observed in TS is due to incorporation of increasing amount of PEG-400 soft segment in the chains, which imparted flexibility of the CPU network. When load is applied to the film, because of high flexibility of soft PEG-400 segment, load is thrown away to the rigid PEP segment of CPU and as a result stress is concentrated at the junction of rigid and soft segments resulting in rupture at low load. Thus, due to lack of mutual coordination between hard and soft segments results non-uniform stress distribution and hence caused decrease in mechanical properties especially TS.

Decrease in ES and VR of CPU is due to increasing amount of soft segment, cross-link density

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characteristic IR frequencies, cm$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>PEP</td>
<td>3423.9 -OH str. 1732.9 (C=O str. 1248.8 C-O ester and ether str.</td>
</tr>
<tr>
<td>PU</td>
<td>3343.4 N-H and -OH str. 1732.0 -C=O urethane str. 1246.9 -C-O urethane and ether str.</td>
</tr>
<tr>
<td>PU-20</td>
<td>4.4 N-H and -OH str. 2.2 -C=O urethane str. 1229.5 -C-O urethane and ether</td>
</tr>
<tr>
<td>PU-30</td>
<td>9.9 N-H and OH str. 2.2 -C=O urethane str. 1230.5 -C-O urethane and ether str.</td>
</tr>
</tbody>
</table>

Table 1 — Characteristic IR absorption frequencies of cardo polyester polyol, PU, PU-20 and PU-30
Table 2 — Properties of PU-20 and PU-30

<table>
<thead>
<tr>
<th>Polyurethane film</th>
<th>TSMPa</th>
<th>ESkV/mm</th>
<th>VROhm cm</th>
<th>$T_o$</th>
<th>$T_{10}$</th>
<th>$T_{50}$</th>
<th>Decomposition range °C</th>
<th>Weight loss, %</th>
</tr>
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<tbody>
<tr>
<td>PU-20</td>
<td>33.0</td>
<td>57.2</td>
<td>$4.6 \times 10^{12}$</td>
<td>190</td>
<td>225.1</td>
<td>362.6</td>
<td>190-304</td>
<td>27.7</td>
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<td></td>
<td></td>
<td>472-540</td>
<td>11.7</td>
</tr>
<tr>
<td>PU-30</td>
<td>4.5</td>
<td>43.1</td>
<td>$2.7 \times 10^{12}$</td>
<td>198</td>
<td>235.5</td>
<td>369.0</td>
<td>198-307</td>
<td>26.1</td>
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<td>350-430</td>
<td>31.6</td>
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<td></td>
<td></td>
<td>488-590</td>
<td>18.4</td>
</tr>
</tbody>
</table>

TS, Tensile strength; ES, Electric strength; VR, Volume resistivity; $T_o$, Initial decomposition temperature; $T_{10}$, Temperature of 10% decomposition; $T_{50}$, Temperature of 50% decomposition.