Polyurethane coatings using trimer of isophorone diisocyanate†

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A trimer of isophorone diisocyanate (IPDI) was prepared considering its industrial applications and safety associated with it was compared to normal diisocyanates. The IPDI trimer has been characterized by PMR and IR spectroscopies, physical constant (melting point) and isocyanate content. This trimer was used for preparing polyurethane cast films as well as coatings using polyether polyols/polyethylene glycols (PEG) of varying molecular weights (PEG 200, 300, 400, 600). After conditioning the samples were subjected to various tests pertaining to coating such as, gloss, scratch resistance and flexibility, while mechanical tests include tensile strength, per cent elongation, Young’s modulus and hardness and the performance are compared in the light of the molecular weight of PEG. Chemical resistance of these samples has been studied in industrially important acids, alkalis, and solvents and swelling characteristics are also studied.

Keywords: Polyurethane coating, Isocyanate trimer, Mechanical properties

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1 Introduction

Polyurethanes (PUs) are most versatile group of industrially important polymers in today’s world. It has applications in various fields like, coatings, paints, foams, elastomers, and adhesives. Because of the excellent properties, its industrial applications as a coatings are increasing every day. Also it is possible to get tailor made properties from PU.1

Monomeric diisocyanates that have high vapor pressure are strong irritants to the mucous membranes the skin and eyes. Constant inhalation of their vapor can lead to asthma. Therefore, isocyanates are pre-reacted to give a safer form useful in commercial surface coatings. The easiest and safer way is to prepare prepolymer or blocked diisocyanate 2,3 to minimize the problem of vapour pressure and toxicity but further problem associated with the use of prepolymer is its higher viscosity and the need for addition of solvents to adjust the viscosity, resulting in increase in the volatile organic content (VOC), that poses problems to the environment.4 Blocked diisocyanates require higher temperature to open the block site and to effect curing.5 To overcome these problems the use of trimer of diisocyanate/s is recommended for industrial coating. Moreover, thermal stability of PUs increases due to the presence of isocyanurate ring, being a heterocyclic one.6,7 The used trimer is expected to impart better cross-linking to the coating in the polymer network in the presence of isocyanurate ring. Linear polyether polyols are preferred in coatings because they are less expensive and impart chain flexibility to the polyurethane coating.

In the present study, we have synthesized a trimer of isophorone diisocyanate (IPDI) using choline hydroxide as a catalyst.9,10 Reaction conditions were optimized for temperature and concentration of the catalyst. The other catalysts recommended include amines, salts of weak acids, potassium acetate, sodium carbonate, and epoxides in the presence of tertiary amines.11-13 The synthesized trimer was characterized by PMR, IR spectroscopies, melting point, and isocyanate value. Literature pertaining to the trimerization of prepolymer and mono isocyanate is available, however, reports on trimerization of diisocyanates are hardly available and most of the information is patented.2,3

Polyurethane coatings and sheets were prepared by reacting trimer with various polyether polyols (PEG) by casting technique. PEG constitutes the soft segment, whereas the hard segment is contributed by

Table 1—Characteristics of PEG and trimer
Materials and Methods

2.1 Materials

PEG - 200, 300, 400 and 600 (S D Fine Chemicals Ltd, Mumbai, India), dibutyltin dilaurate (DBTDL) (Aldrich Chemicals, India/USA) were of laboratory grade chemicals. The PEGs were characterized by hydroxyl value and viscosity. IPDI (Kishore Polyurethanes Pvt Ltd, Nashik, India) was of commercial grade, used as such. The IPDI was characterized by determining isocyanate content. The characteristics results of PEGs and trimer (IPDI) are summarized in Table 1.

2.2 Hydroxyl Value

Hydroxyl value of all PEGs was determined by reacting it with acetylating reagent (acetic anhydride and pyridine mixture) and the excess acetic anhydride was hydrolyzed and titrated with alcoholic KOH as per the procedure recommended by ISI:354 (1987).

2.3 Viscosity

Viscosity of PEG and trimer was measured on Brookfield viscometer (Brookfield Engineering Laboratories Inc., USA, Model LV), by selecting appropriate spindle and speed for particular viscosity as per the procedure recommended by ASTM D 2849 (1980).

2.4 Isocyanate Value

It is tested by reacting trimer with excess n-dibutylamine and titrating unreacted dibutylamine with hydrochloric acid. 17

2.5 Synthesis of Catalyst (Choline hydroxide)

Choline hydroxide, used as a catalyst for the synthesis of IPDI trimer, was synthesized in the laboratory from choline chloride 18,19, choline chloride was synthesized from trimethylamine and ethylene chlorohydrin, which was further treated in situ with KOH in ethanol : 2-hydroxy ethyl hexanol (1:8) mixture (Scheme 1). The precipitated KCl was separated by filtration and filtrate was diluted to 10 per cent choline hydroxide with above solvents mixture and then utilized as a catalyst for trimerization of IPDI.

2.6 Dibutyltin Dilaurate (DBTDL)

DBTDL is well known commercially available catalyst used for the synthesis of polyurethanes. 20 It was diluted to 10 per cent with dry THF and used for the synthesis of polyurethane coatings and sheets.

2.7 Synthesis of Trimer of IPDI

The isocyanate content of the trimer was found to be 9.8 per cent and viscosity of trimer was 730 cps.
A general reaction of trimerization of isophorone diisocyanate and the possible structure of trimer is presented in Scheme 2. Four-necked 500 mL resin kettle was equipped with nitrogen gas, thermometer, dropping funnel, mechanical stirrer, and water condenser. Whole assembly was placed in an oil bath at 75°C. After flushing reactor with nitrogen (for 10 min), IPDI (100 g) was charged and stirred for 15 min to attain the ambient temperature (75°C). Then diluted solution of choline hydroxide catalyst (9 mL) was added dropwise. The reaction was monitored by measuring isocyanate content for about 6-8 h until the isocyanate content became half of the initial quantity. Then catalyst was deactivated by adding appropriate quantity of toluene sulphonic acid using DMF as solvent. In this case, amount of DMF, added is negligible and will not affect on isocyanate value.

2.8 Preparation of PU Coating Panels and Sheets

PEG was first degassed and then reacted at 50°C with IPDI trimer in a three-necked flask, equipped with mechanical stirrer and immersed in oil bath. The catalyst DBTDL was added to polyol, instead of adding to the mixture of polyol and trimer, to control the reaction rate. Stirring was continued till a viscous pourable mass was obtained which was transferred to a preheated coating panels and steel plates. Initially the material was cured at 50°C under vacuum to remove the solvent and to degas the mass. After releasing vacuum it was again cured at 50°C for 12 h. Coating panels were used as such to study coating properties while the films 3-4 mm thick were collected from steel plate to study mechanical properties by cutting dumbbell shape of specimen using a die. The samples were coded as PU-200, PU-300, PU-400 and PU-600 the number indicates molecular weight of corresponding PEG used.
2.9 Coating Properties

The coating properties such as, gloss, scratch resistance, and flexibility of these polyurethanes were studied (Table 2).

2.9.1 Gloss

Gloss was measured at an angle of 45° on digital gloss meter ‘RSPT – 20’ (Rajdhani Pvt. Ltd, India).

2.9.2 Scratch Resistance

Scratch resistance of all coating samples was measured on ‘Automatic Scratch Tester’, (Rajdhani Pvt Ltd, India).

2.9.3 Flexibility

Flexibility of coating panels was measured at an angle of 180°, using conical mandrel, Petroleum Instruments Pvt Ltd, Calcutta, India.

2.10 Mechanical Properties

Dumbbells shaped specimens were tested for mechanical properties such as, tensile strength, Young’s modulus, and per cent elongation. These samples were tested on computer controlled Universal Tensile
Machine (R & D Equipment, Mumbai, India Model No UT 2302) using ASTM D 638 method. Shore hardness (Shore A) was measured on shore hardness tester (Blue Steel, India) by ASTM D 2240 method.

2.11 Chemical Resistance

The coatings always come in contact with various industrially important chemicals, thus a study of chemical resistance of these PU sheets was considered (sulphuric acid, acetic acid, hydrochloric acid, nitric acid, sodium chloride, sodium hydroxide, ammonium hydroxide, methyl ethyl ketone (MEK), carbon tetrachloride, chloroform, toluene, and distilled water) according to ASTM D 543-67 (1972) method, samples were suspended in the reagent for 7 d and tested for change in weight and in appearance.

2.12 Solvent Absorption

As these coatings come in contact with many industrial solvents, it is very essential to know about solvent absorption in common industrial solvents. This capacity is assessed by the solvent absorption and expressed as the amount of liquid absorbed by unit mass or volume of the polymer. Solvent absorption was measured by immersing a piece of PU samples in test solvents. The specimens were weighed at appropriate time intervals and constancy in the weight was considered for judging the equilibrium. The solvent absorption was calculated using following formula:

\[
\text{Per cent solvent absorption} = \frac{\text{Weight of(Swollen polymer – Dry polymer)}}{\text{Weight of dry polymer}} \times 100
\]

3 Results and Discussion

The present study aims at the synthesis and characterization of trimer, preparation of PU coatings and their physicochemical testing. An attempt was made to prepare polyurethane samples, based on trimer as well as the diisocyanate for the sake of comparison but PU samples of the diisocyanate could not be obtained in solid sheet form as they were sticky in nature. Hence the results of PUs prepared by using trimer (IPDI) are only discussed here.

3.1 Melting Point of Trimer

The melting point of synthesized trimer was determined by open capillary method and found to be in the range of 70–75°C.

3.2 Spectroscopic Characterization

The synthesized trimer was characterized by PMR and IR spectroscopic techniques.

3.2.1 PMR (CDCl3, δ ppm) –

0.50 – 1.32 [m, CH3 (c, g)], 1.32 – 1.65 [m, CH2 (b)],
1.70 – 2.25 [m, CH2 (d, f)], 3.35 – 3.64 [m, CH2 (a)],
4.05 – 4.41 [m, CH (ε)]

3.2.2 IR (KBr, cm⁻¹)
3.3 Coating Properties

The tested coating properties include gloss, scratch resistance and flexibility. Gloss of all the PU samples was between 56-57 and no abnormal change was found. Scratch resistance of polyurethane coatings was found between 200-300 g and remained same for all the samples. Samples were passed without any crack or break on the film during the flexibility test.

3.4 Mechanical Properties

Mechanical properties such as, tensile strength, elongation at break (per cent), Young’s modulus and hardness are given in Table 3.

It is evident that tensile strength of PU increases as molecular weight of PEG decreases. This increase in tensile strength is due to the decrease in length of soft segment (PEG) and increase in percentage of urethane in the main chain. It is seen that elongation is increased on increasing molecular weight of PEG. This increase in elongation is due to the increase in length of soft segment that imparts flexibility. It is observed that on increasing molecular weight of PEG the magnitude of Young’s modulus is found to decrease, as expected, and increased length of the soft segment is responsible for higher elongation.

The decrease in hardness is found on increasing the molecular weight of the soft segment in accordance with the theory.

Table 3—Mechanical properties

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Property</th>
<th>Polyurethanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tensile strength (Psi)</td>
<td>PU-200 812</td>
</tr>
<tr>
<td>2</td>
<td>Elongation at break, per cent</td>
<td>18.17</td>
</tr>
<tr>
<td>3</td>
<td>Young’s modulus (Psi)</td>
<td>PU-300 783</td>
</tr>
<tr>
<td>4</td>
<td>Shore A hardness</td>
<td>PU-400 754</td>
</tr>
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</table>

Table 4—Chemical resistance

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Compound</th>
<th>Polyurethanes (per cent weight loss and estimated error is ±0.002)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PU-200  PU-300  PU-400  PU-600</td>
</tr>
<tr>
<td>1</td>
<td>H_2SO_4, 25 per cent</td>
<td>0.890   1.700   2.310    2.330</td>
</tr>
<tr>
<td>2</td>
<td>HCl, 25 per cent</td>
<td>0.570   1.400   1.340    0.490</td>
</tr>
<tr>
<td>3</td>
<td>HNO_3, 25 per cent</td>
<td>1.440   1.520   2.330    1.490</td>
</tr>
<tr>
<td>4</td>
<td>CH_3COOH, 25 per cent</td>
<td>1.190   1.600   2.670    2.540</td>
</tr>
<tr>
<td>5</td>
<td>NaOH, 10 per cent</td>
<td>0.440   1.420   2.460    1.200</td>
</tr>
<tr>
<td>6</td>
<td>NH_4OH, 10 per cent</td>
<td>0.068   0.075   0.082    0.091</td>
</tr>
<tr>
<td>7</td>
<td>NaCl, 10 per cent</td>
<td>0.710   2.120   2.270    2.110</td>
</tr>
<tr>
<td>8</td>
<td>Distilled water</td>
<td>1.050   1.610   1.780    3.340</td>
</tr>
<tr>
<td>9</td>
<td>MEK</td>
<td>2.260   2.680   1.410    1.210</td>
</tr>
<tr>
<td>10</td>
<td>CCl_4</td>
<td>1.370   2.810   2.730    1.860</td>
</tr>
<tr>
<td>11</td>
<td>CHCl_3</td>
<td>0.850   1.040   3.610    2.890</td>
</tr>
<tr>
<td>12</td>
<td>Toluene</td>
<td>0.600   0.330   2.660    2.470</td>
</tr>
</tbody>
</table>

2956, 2929 (C-H), 2259 (-N=C=O), 1693 (C=O), 1215 (-C-N-)
3.5 Chemical Resistance

The per cent weight loss of polyurethane specimens are summarized in Table 4. All PU samples showed excellent acid, alkali, and solvent resistance and no significant change in the physical appearance of polyurethane samples was seen except in H\textsubscript{2}SO\textsubscript{4} and CHCl\textsubscript{3}. Specimens became soft in sulphuric acid and then slightly yellow when dried. While in chloroform the samples became brittle after drying. Thus, PUs showed good resistance towards acids, alkalis, and solvents too. It is also found that alkali resistance of samples is more than acid resistance. In general, PU-200 has shown better chemical resistance due to increase in hard-core segments.

3.6 Solvent Absorption

Results of solvent absorption are as shown in Table 5. The solvent absorption increased with increase in molecular weight of PEG, which was due to decrease in the percentage of hard segment, imparting lower degree of cross-linking. Higher cross-linking does not allow solvent to penetrate and in the present case of PU-200, less penetration is observed because of higher degree of cross-linking.

4 Conclusions

The present investigation proves that polyurethane coatings prepared in the laboratory show good coating properties without abnormal change in any sample. If the ratio of trimer to PEG is kept constant, tensile strength increase inversely with molecular weight of PEG. Further the elongation of PU depends upon molecular weight of PEG and increased with increase in molecular weight of PEG. Young's modulus of PU is higher at lower molecular weight of PEG and vice versa. It was found that hardness decrease with increase in length of PEG. The chemical resistance of PUs synthesized in various acids, alkalis, and solvents is found to be excellent. Chemical resistance and solvent absorption show that PU samples made by using trimer are cross-linked properly without any additional cross-linking agent.

Thus the use of trimerization of isocyanate exhibit significant enhancement in coatings and their mechanical and chemical properties. Hence the use of trimer, instead of diisocyanate, is desirable for a specific end use requirement in PU coatings.

5 Acknowledgement

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Abbreviation Used
PDI – Isophorone diisocyanate
IPDI – Isophorone diisocyanate