



**Pelagia Research  
Library**

## Pelagia Research Library

Der Chemica Sinica, 2011, 2(5): 54-64



**Pelagia Research  
Library**  
ISSN: 0976-8505  
CODEN (USA) CSHIA5

### Bio-based thermosetting tough polyurethanes

S. Gopalakrishnan\* and T. Linda Fernando

*Department of Pharmaceutical Chemistry, Manonmaniam Sundaranar University,  
Abishekapatti, Tirunelveli, Tamilnadu, India*

---

#### ABSTRACT

*Novel thermosetting polyurethanes from novolac type hydroxyalkylated cardanol-formaldehyde resins, polypropylene glycols (PPG-1200 and PPG-2000) and aliphatic diisocyanates such as hexamethylene diisocyanate and isophorone diisocyanate were prepared in the form of thin sheets. The sorption, mechanical and thermal properties have been studied. The solubility parameters, molecular weight between two crosslinks of the polyurethane samples were calculated from swelling experiments. The swelling study of polyurethanes revealed that the sorption is found to decrease with an increase in chain length of PPG. The stress-strain and thermo analytical data showed the high performance character of the IPDI treated polyurethanes with respect to their mechanical and thermal properties.*

**Keywords:** Cardanol, diisocyanate, polypropylene glycol, tough polyurethane, solubility parameter.

---

#### INTRODUCTION

Renewable organic resources continue to be in the common interest of both academic and industrial laboratories throughout the world at all the times [1-5]. The topic has attained a renewed interest for reasons of economy and environmental friendliness and contributes well to green chemistry practices. Vegetable oils are one of the cheapest and most abundant biological renewable sources available in large quantities, and their use as starting materials has numerous advantages: for example, low toxicity, inherent biodegradability, and high purity [6-7]. Among the renewable sources, Cashew Nut Shell Liquid (CNSL), an agricultural resource material obtained as a byproduct of the cashew industry is unique in that it contains a natural phenolic distillate, cardanol [8]. Considerable attention from polymer scientists is devoted to utilize their potential attributes as a substitute for petrochemical derivatives and they are considered to be one of the most important classes of renewable sources for the production of bio-based thermosetting polyurethanes [9-11]. Polyurethanes are a unique class of polymers that have a wide range of applications because their properties can be readily tailored by the variations of their components. Thus polyurethanes provide a versatile range of properties and find extensive applications especially in the biomedical field which include synthesis of catheters of wide

range[12],pacemaker lead insulation[13], polyurethanes vascular grafts[14]and artificial heart valves[15].A favourable feature associated with polyurethane system is the ease with which the end property can be tailored with good control by mere adjustment in the formulation.

Vegetable oil- based polyols have been widely used to produce segmented and non segmented polyurethanes [16-21]. Segmented polyurethanes are elastomeric block copolymers that generally exhibit a phase-segregated morphology made up of soft rubbery segments and hard glassy or semicrystalline segments [22]. The soft segment usually consists of polyether or polyester diols whereas the hard segment consists of the diisocyanate component and a low molecular weight chain extender. The advantage of segmented polyurethanes is that their segmental and domain structure can be controlled over a considerable range through the selection of the materials, their relative proportions, and the processing conditions.

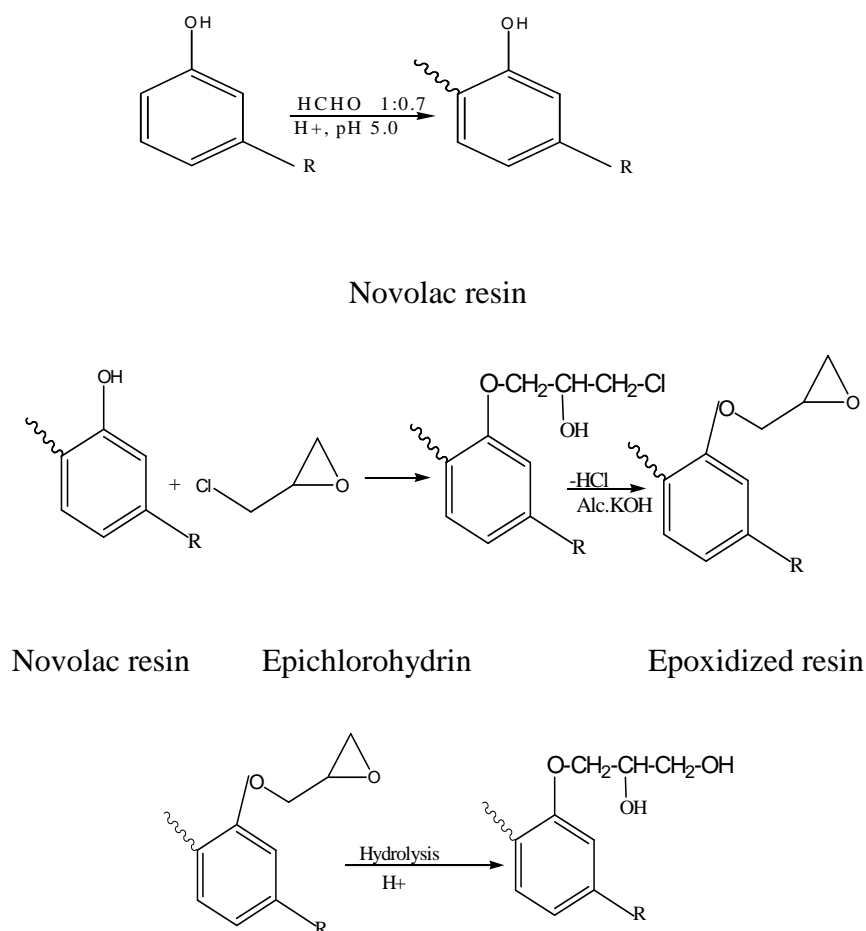
In the present study, cardanol has been made to react with formaldehyde in the mole ratio 1:0.7 in the presence of sebacic acid catalyst, a dicarboxylic acid to form cardanol - formaldehyde resin. The resulting methylolated cardanol-formaldehyde resin is properly modified to a high molecular weight hydroxyalkylated derivative, through epoxidation followed by hydrolysis. Such a nucleophilic high molecular weight polyol is allowed to condense with aliphatic diisocyanates(HDI and IPDI) and commercially available polyols such as polypropylene glycols PPG-1200 and PPG-2000 to get the tough polyurethanes.

## MATERIALS AND METHODS

Cardanol was procured from M/s Sathya Cashew Pvt. Ltd., Chennai. Formaldehyde (40% solution) for formylation and methanol for dissolving the catalyst were obtained from M/s BDH Ltd. Sebacic acid and epichlorohydrin were received from M/s E.Merck,Germany. Polypropylene glycols (PPG) of molecular weight 1200 and 2000 used in the study were purchased from Aldrich Chemicals (USA) and were dried over anhydrous  $\text{Na}_2\text{SO}_4$  to remove traces of water. All the solvents used were of analytical grade and were further purified by distillation. Hexamethylene diisocyanate (HDI), Isophorone diisocyanate (IPDI) and the catalyst dibutyltin dilaurate (DBTDL) were received from Fluka Chemie (UK) and used as received.

### 2.2. Synthesis of bio-based polyol

High ortho multinuclear cardanol - formaldehyde resin was synthesized using cardanol: formaldehyde in the mole ratio 1:0.7 using sebacic acid as catalyst. Cardanol was taken in a three necked round bottomed flask equipped with a Liebig condenser, mechanical stirrer and thermometer. Formaldehyde and 1% sebacic acid catalyst in methanol (2 ml) was added to the cardanol through a dropping funnel. The reaction was carried out at temperature  $120^\circ \pm 5^\circ\text{C}$  for 3 hours and then at  $150^\circ \pm 5^\circ\text{C}$  for 2 h. The initial pH value of the mixture was lowered from 5 to 3 after the completion of the condensation. The resin was purified by dissolving in toluene and then by precipitating it with distilled water. Major fractions were collected and dried using a rotary evaporator under vacuum. The cardanol-formaldehyde resin was epoxidized using epichlorohydrin and the resulting epoxidized resin was hydrolysed with dilute hydrochloric acid. The hydroxyalkylated resin (synthesized polyol) thus formed was purified by washing with distilled water several times and then dried over vacuum at  $80^\circ\text{C}$  (Scheme 1).



**Scheme 1: Formation of synthesized polyol**

### 2.3. Synthesis of polyurethanes

In this study, novel biobased polyurethanes were prepared in the form of thin sheets using transfer molding technique. The polyurethanes (HPU<sub>1</sub> and HPU<sub>2</sub>) were synthesized by blending the vacuum dried cardanol-formaldehyde resin, hexamethylene diisocyanate and the commercially available polyols, polypropylene glycol-1200/ polypropylene glycol-2000 followed by the addition of the catalyst DBTDL (0.01 wt.% total charge) at room temperature. All these ingredients were mixed well in a small cup and poured into a flat iron mould. The completion of the reaction was indicated by the absence of air bubbles. The polyurethane sheets formed were allowed to stand for 24 h, demoulded and cured in a vacuum oven at 110°C for 48 h. The polyurethane sheets (IPU<sub>1</sub> and IPU<sub>2</sub>) were synthesized by blending the cardanol-based polyol, with required quantities of PPG-1200 and PPG-2000 respectively along with isophorone diisocyanate and the catalyst at 75°C by adopting similar experimental procedure as discussed for the synthesis for HPU<sub>1</sub> and HPU<sub>2</sub>. In both the cases, the isocyanate index was fixed as 1.4.

### 2.4. Static contact angle (SCA)

Contact angle provides information on the surface hydrophilicity/ hydrophobicity and molecular mobility at the air-solid-water interface [23]. The static contact angles of synthesized polyurethane were measured using Rame Hart Goniometer (Model 100-00-230). Static contact angle measurement analysis was performed by depositing 1 ml droplets of de-ionized water onto the surface of polyurethane sheet and taking photos through a magnifying lens using a digital camera. This process was repeated 8–10 times for each sample. The height *h* and the length *l* of

the droplet were measured and the static contact angle between the droplet and the coated surface calculated using the equation  $\tan(\theta/2) = 2h/l$ , where  $\theta$  is the static contact angle in degrees.

### 2.5. Swelling experiments

Equilibrium swelling experiments were performed at 30°C to determine solubility parameter of polyurethane samples. In the swelling experiments, a so-called pat and weight technique was used for liquid sorption [24]. Samples, after taking the dry weight, were placed in dimethyl acetamide in a standard joint test tube, which was maintained at a temperature of 30°C. The specimens were taken out at regular intervals and solvents adhering to the surface was rubbed off, weighed immediately, and replaced in solvent. This was repeated for three specimens from each network in order to ensure the reproducibility of the values. The time taken for wiping out the solvent from the sample surface was kept to a minimum in order to minimize error due to solvent evaporation. The swelling coefficient 'Q' was calculated using the formula,

$$Q = \frac{\text{Weight of solvent in swelled polymer} \times d_s}{\text{Weight of the polymer subjected to swelling} \times d_r}$$

Where,

$d_s$  = Density of solvent

$d_r$  = Density of polymer

The solubility parameters of solvents were plotted against the swelling coefficient of the polyurethanes. The peak of the curve gives the solubility parameter of the polyurethanes. The densities of polymer films were determined by a floatation method.

The crosslink density was determined using modified Flory - Rehner equation [25],

$$\gamma = \frac{V_r + \chi V_r^2 + \ln(1-V_r)}{d_r V_o (V_r^{1/3} - V_r/2)} = \frac{1}{M_c}$$

Where,

$V_r$  = Volume fraction of polyurethane in swollen polymer i.e.  $V_r = 1/1+Q$

Q = Swelling coefficient

$V_o$  = Molar volume of the solvent

$M_c$  = Molecular weight between two cross links

$d_r$  = Density of polyurethane.

$\chi$  = Polymer - solvent interaction parameter which was calculated using the equation [26],

$$\chi = \frac{\beta + V_s (\delta_s - \delta_p)^2}{RT}$$

Where  $V_s$  = Molar volume of solvent

R = Gas Constant

$\delta_s$  = Solubility parameter of DMA

$\delta_p$  = Solubility parameter of polyurethane

T = Absolute temperature

$\beta$  = Lattice constant which is generally taken as 0.34 for good solvent

When  $\delta_s = \delta_p$ , the polymer-solvent interaction parameter ( $\chi$ ) becomes equal to the lattice constant ( $\beta$ ).

Using solvent interaction parameter ( $\chi$ ), the crosslink density of the polyurethanes is determined.

## 2.6. Mechanical testing

Cured polyurethane samples were kept in the vacuum oven overnight. According to ASTM -D 412 specifications, dumb-bell specimens were cut out from polyurethane sheets and the tensile strength, percentage elongation and modulus were determined using universal tensile testing machine. Indentation hardness (Shore-A) hardness of all the samples was measured by means of a type A Shore durometer at room temperature as per ASTM- A 2240.

## 2.7. Thermal properties

The thermal properties of the polyurethanes were studied by differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) at a rate of 20°C/min in nitrogen using Universal V4.3A Instruments.

Activation energy ( $E_a$ ), which is a quantitative measure of thermal stability associated with each stage of decomposition evaluated by the well-known Broido method [27], can be calculated by using

$$\ln \ln \left( \frac{1}{Y} \right) = \left( \frac{-E_a}{R} \right) \frac{1}{T} + \text{Constant}$$

Where

$$Y = \frac{W_t - W_\infty}{W_0 - W_\infty}$$

Y = fraction of the number of initial molecules not yet decomposed

$W_t$ - the weight at anytime t

$W_\infty$ - the weight at infinite time (= zero)

$W_0$ - the initial weight of the sample

A plot of  $\ln[\ln(1/Y)]$  vs.  $1/T$  gives an excellent approximation to a straight line. From the slope, activation energy  $E_a$  is calculated by multiplying with gas constant R.

## RESULTS AND DISCUSSION

Polyurethanes prepared by a transfer molding technique were in the form of thin amber coloured sheets. PPG-1200 based polyurethanes (HPU<sub>1</sub> and IPU<sub>1</sub>) were found to be soft and the PPG-2000 based polyurethane (HPU<sub>2</sub> and IPU<sub>2</sub>) were found to be soft and sticky.

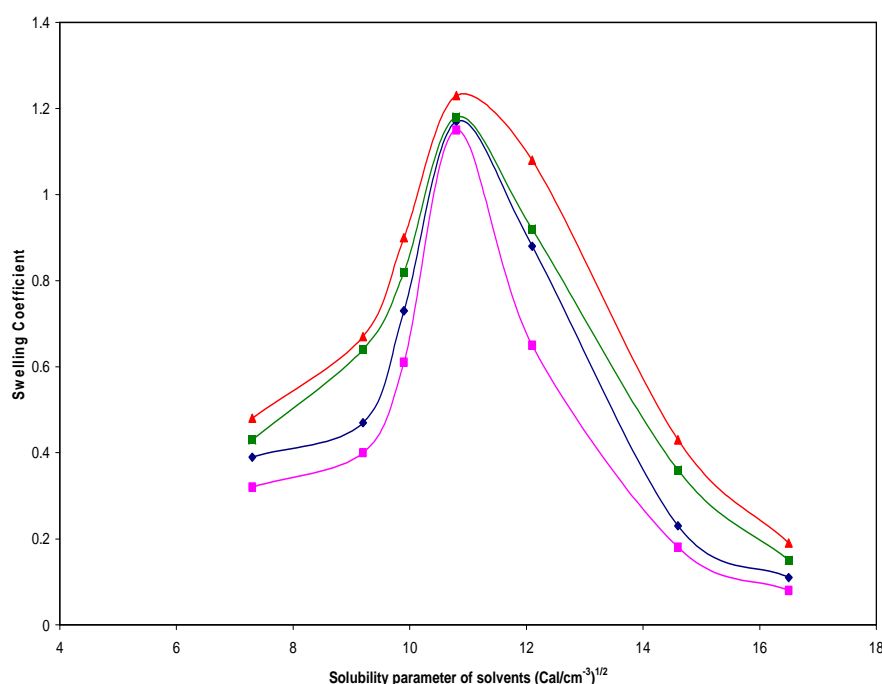
### 3.1. Static contact angle measurement

Surface hydrophilicity of polyurethane sheets is very important for water selectivity. Contact angle decreased with increasing length of PPG soft segment. A higher contact angle value represents a more hydrophobic surface [28]. PPG-1200 based polyurethanes (HPU<sub>1</sub> and IPU<sub>1</sub>) showed higher contact angle value than those of PPG-2000 based polyurethanes (HPU<sub>2</sub> and IPU<sub>2</sub>) (Table 1). The reason for the low contact angle value of HPU<sub>2</sub> and IPU<sub>2</sub> are attributed to

the presence of long flexible hydrophilic soft segment of PPG-2000 with large number of -OH groups.

### 3.2. Swelling characteristics and crosslink density

The swelling measurements of the polyurethanes have been carried out in various solvents having different solubility parameters value ( $\delta$ ) ranging from 7.3 to 16.5 (cal/cm<sup>3</sup>)<sup>1/2</sup>. When the solubility parameters of solvents were plotted against the swelling coefficient of the polyurethanes, a maximum in the peak corresponding to the solubility parameter of dimethyl acetamide was obtained (Figure 1). Among all the solvents used, the solubility parameter of dimethyl acetamide ( $\delta_s$ ) was found to be the solubility parameter of polyurethanes, as there was maximum swelling only in this solvent. The swelling properties of these polyurethanes reveal that the present polyurethanes are cross linked. These crosslinked polymers will only swell and do not dissolve in a non reactive solvent.



**Fig. 1.** Swelling coefficient curves of polyurethanes

The degree of swelling in a non reactive solvent determines the degree of cross linking and hence the molecular weight between cross links ( $M_c$ ). Higher the  $M_c$ , lower will be the crosslink density.

In the present investigation, the crosslink density of HPU<sub>1</sub> and IPU<sub>1</sub> are found to be higher in comparison with those prepared with the addition of commercial polyol, PPG-2000 (Table 1). Accordingly the molecular weight between crosslinks,  $M_c$  is also found to be minimum in these cases.

It has been reported that, as the distance between two crosslink points increases with an increase in chain length (for a given NCO/OH ratio) of highly flexible PPG,

**Table 1: Physical parameters of polyurethanes**

| Polyurethane code | Density (g/cc) | Swelling coefficient in DMA (Q) | Volume fraction of polyurethane ( $V_r$ ) | Cross link density $\times 10^{-3}$ | Molecular weight between cross links ( $\text{mole}^{-1}$ ) | Contact angle |
|-------------------|----------------|---------------------------------|---|-------------------------------------|---|---------------|
| HPU <sub>1</sub>  | 1.11           | 1.40                            | 0.714                                     | 0.879                               | 813.72  | 70°           |
| IPU <sub>1</sub>  | 1.08           | 1.43                            | 0.699                                     | 0.995                               | 771.82  | 66°           |
| HPU <sub>2</sub>  | 1.04           | 1.55                            | 0.645                                     | 0.755                               | 883.74  | 62°           |
| IPU <sub>2</sub>  | 1.02           | 1.49                            | 0.671                                     | 0.772                               | 892.03  | 65°           |

the free volume available also increases and hence the volume fraction of polyurethane in swollen polymer ( $V_r$ ) decreases [29]. The increase in chain length increases the distance between two crosslink points resulting in a less dense crosslinked structure. Therefore  $M_c$  increases with the increase in molecular weight of PPG.

### 3.3. Mechanical properties

The tensile properties in terms of tensile strength, modulus and percentage elongation evaluated from stress-strain curves are tabulated in Table 2. In the case of higher molecular weight polyol-based polyurethanes HPU<sub>2</sub> and IPU<sub>2</sub>, there is an unequal distribution of load throughout the network due to its low crosslink density and due to the presence of longer chain length of the soft segment PPG-2000. When the load is applied to the polymer network of PPG-2000 based polyurethanes, because of its high flexibility throw away the load to the rigid part of the network and creates stress concentration at that region. Ultimately, rupture takes place even at low load resulting in a decrease in tensile strength. However, in the case of PPG-1200 added polyurethanes, the shorter length of flexible chain contributes to bare load along with the rigid hard segment region coordinately which leads to an increase in tensile properties. Hardness of polyurethane samples is also shown in Table 2.

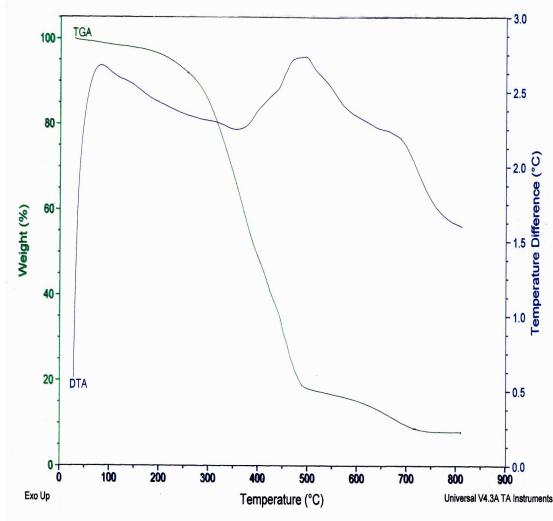
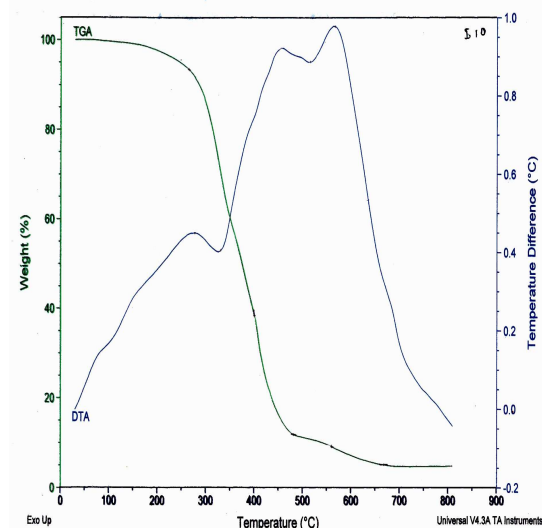
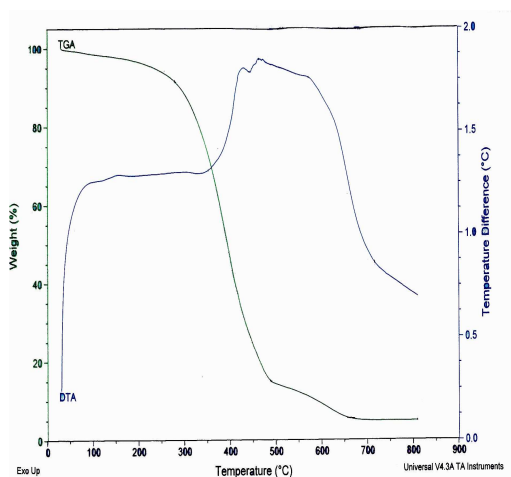
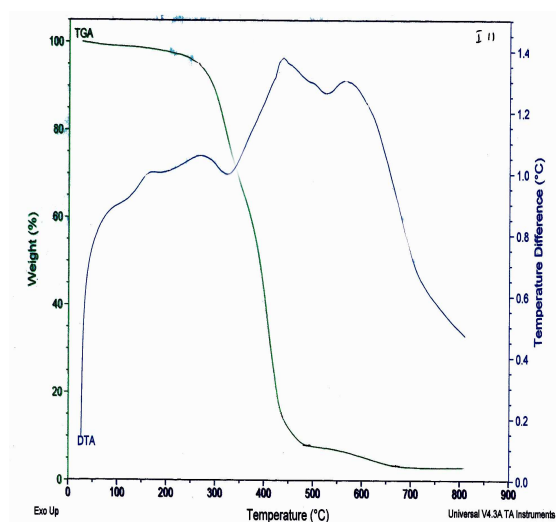
**Table 2 Mechanical properties of polyurethanes**

| Polyurethane code | Shore A hardness | Tensile strength (MPa) | Elongation (%) | Tensile modulus (MPa) |
|-------------------|------------------|------------------------|----------------|-----------------------|
| HPU <sub>1</sub>  | 83               | 35.4                   | 123            | 28.7                  |
| IPU <sub>1</sub>  | 90               | 30.1                   | 139            | 21.7                  |
| HPU <sub>2</sub>  | 60               | 25.0                   | 154            | 16.2                  |
| IPU <sub>2</sub>  | 72               | 32.8                   | 129            | 25.4                  |

As can be seen from the Table 2, hardness of polyurethane increases with a decrease in the chain length of PPG. This is due to the fact that as chain length is decreased, crosslink density increases, which results into more rigid network with better mechanical properties. The shore-A hardness values of IPDI treated polyurethanes are found to be more than those of HDI treated ones. This may be attributed to the high crosslink density of IPDI treated polyurethanes resulting from the unsymmetrical structure of IPDI.

### 3.4. Thermal properties

The thermograms of polyurethane samples are shown in Figure 2 - Figure 5 and the TGA and DTA analysis data of polyurethanes are presented in Table 3 and Table 4 respectively.

Fig.2. TGA and DTA Curves of HPU<sub>1</sub>Fig. 3. TGA and DTA Curves of IPU<sub>1</sub>Fig.4. TGA and DTA Curves of HPU<sub>2</sub>Fig. 5. TGA and DTA Curves of IPU<sub>2</sub>

The DTA curves of polyurethanes do not show any endothermic peak for softening. But two exotherms are invariably seen in all the cured polyurethanes. The first exotherm is relatively weak and the second exotherm is strong in all the four polyurethanes. The first exotherm is due to the cleavage of meta - substituted long alkyl side chain of the phenyl ring and also due to the cleavage of allophanate linkages. The third exotherm of IPDI treated polyurethanes occur at higher temperatures (739°C and 696°C) than those of the HDI treated polyurethanes HPU<sub>1</sub> and HPU<sub>2</sub> which occur at 588°C and at 557°C respectively.

Table 3 Differential Thermal Analysis data of polyurethanes

| Polyurethane code | Exotherm (°C) |        |            |
|-------------------|---------------|--------|------------|
|                   | First         | Second | Third      |
| HPU <sub>1</sub>  | 172           | 467    | 588        |
| IPU <sub>1</sub>  | 253           | 450    | <b>739</b> |
| HPU <sub>2</sub>  | 254           | 481    | 557        |
| IPU <sub>2</sub>  | 282           | 490    | <b>696</b> |

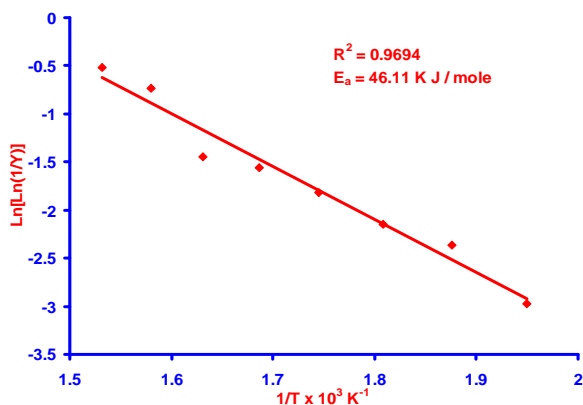
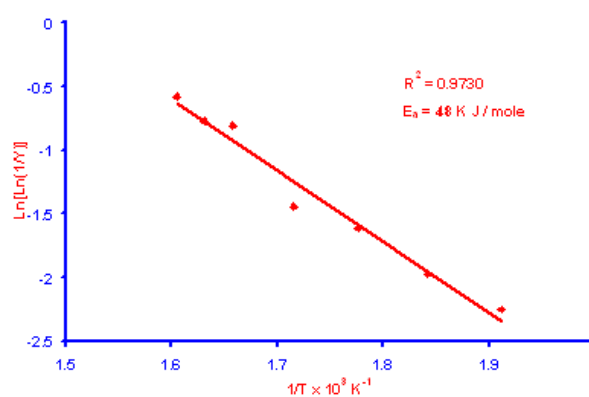


**Table 4** Thermo Gravimetric Analysis data of polyurethanes

| Polyurethane code | Weight loss at various temperatures ( °C) |     |     |     |     | Char residue (%)<br>800 °C |
|-------------------|---|-----|-----|-----|-----|----------------------------|
|                   | 100                                       | 200 | 300 | 400 | 500 |                            |
| HPU <sub>1</sub>  | 0   | 0.5 | 15  | 35  | 84  | 0.35                       |
| IPU <sub>1</sub>  | 0   | 3   | 13  | 44  | 75  | 3.20                       |
| HPU <sub>2</sub>  | 0   | 2   | 15  | 31  | 86  | 0.26                       |
| IPU <sub>2</sub>  | 0   | 1   | 14  | 29  | 79  | 2.28                       |

The TGA curves of polyurethanes show that these polyurethanes decompose in two or three distinct stages. As can be seen from the thermograms, all the polyurethane samples, regardless of the chain length of polyol used, undergo spontaneous decomposition around 270°C. Once the degradation has started, weight loss is rapid. The initial weight loss (about 5%) up to 200 °C is attributed to the moisture retained in the sample. The IPDI treated polyurethanes decompose around 75-79% at 500 °C, but at the same temperature the polyurethanes based on HDI decompose around 84-86% thereby showing the higher thermal stability of the former. The first break of the TG curves around 270 °C is due to the decrosslinking or post curing process. The second break around 380 °C-400 °C indicates the decomposition of polyurethane moiety of the compound. And the last break around 500 °C is due to disintegration of the resin moiety into simpler molecules.

The typical char is a carbonaceous material that forms during thermal degradation. It has been reported that [30] char yield as determined from TGA experiments are an indirect way of measuring the fire retardant property or in other words thermal stability. Higher the char residue percentage more will be the thermal stability. The percentage of char residue is found to be more in the case of IPDI treated polyurethanes thereby showing the higher thermal stability of the former. Moreover crosslink density of polyurethane samples is linearly changing with thermal stability. From the data, it is very clear that the IPDI treated polyurethanes based on PPG-1200 possess the highest thermal stability than the other three.

**Fig. 6.** Representative Broido plot of HPU<sub>1</sub>**Fig. 7.** Representative Broido plot of IPU<sub>1</sub>

Representative Broido plots of HPU<sub>1</sub> and IPU<sub>1</sub> are shown in Figure 6 and Figure 7 respectively and the values of the activation energy of decomposition of the polyurethanes calculated by Broido method are presented in Table 5. From the Table it has been inferred that, the energy of activation ( $E_a$ ) is higher for the first stage than the second stage of degradation in all the polyurethanes studied using Broido method. This shows that first step is the slowest step. This may be due to the fact that, decrosslinking of the long alkyl side chain occurs in the first stage, followed by the rapid decomposition of polyurethane moiety in the second step.

**Table 5 Kinetic parameters for the thermal degradation of polyurethanes**

| Polyurethane code | Decomposition Temperature range (°C) | R <sup>2</sup> | Activation energy KJ/mol |
|-------------------|--------------------------------------|----------------|--------------------------|
| HPU <sub>1</sub>  | 260 - 350                            | 0.9694         | 46.11                    |
|                   | 380 - 500                            | 0.8884         | 40.7                     |
| IPU <sub>1</sub>  | 260 - 360                            | 0.9730         | 48.0                     |
|                   | 380 - 520                            | 0.9669         | 42.0                     |
| HPU <sub>2</sub>  | 250 - 340                            | 0.9730         | 41.0                     |
|                   | 360 - 520                            | 0.9102         | 39.3                     |
| IPU <sub>2</sub>  | 270-350                              | 0.9730         | 46.1                     |
|                   | 370-530                              | 0.9113         | 40.1                     |

The energy of activation ( $E_a$ ) values of IPDI treated polyurethanes are found to be higher than those of HDI treated polyurethanes. This may be attributed to the higher crosslink density of IPDI treated polyurethanes which require more energy to break the core structure when compared to that of HDI treated polyurethanes which are having lesser crosslink density due to its linear flexible structure. In the same way higher molecular weight polyol added polyurethanes HPU<sub>2</sub> and IPU<sub>2</sub>, are found to possess lower  $E_a$  values than those of HPU<sub>1</sub> and IPU<sub>1</sub>, which may be attributed to the lower crosslink density resulting from the increased chain length of PPG-2000 incorporated polyurethanes.

## CONCLUSION

Polyurethanes synthesized from cardanol-based polyol, aliphatic diisocyanates and linear polypropylene glycols were thin sheets with soft and highly flexible characters depending on the nature and molecular weight of the polyols. Sorption coefficients were found to be dependent on the crosslink density and structure of the network. Among all the tough polyurethanes, PPG-1200 added polyurethanes are found to be more stable than those derived from the PPG-2000 added ones. IPDI treated polyurethanes showed the best mechanical and thermal properties than the HDI treated analogues.

## REFERENCES

- [1] L.H. Sperling, J.A. Manson, S. Qureshi, A. M. Fernandez. *Ind. Eng. Chem. Prod. Res. Dev.*, **1981**, 20: 163.
- [2] Y. Chen, L. Zhang, L. Du, *Ind. Eng. Chem. Res.*, **2003**, 42: 6786.
- [3] P.T. Anastas, M. Kirchoff, M. Origin, *Acc. Chem. Res.*, **2002**, 35: 686.
- [4] R. Hofer, P. Daute, R. Gruetzmacher, A. Westfechtel *J. Coat. Technol.*, **1997**, 69: 65.
- [5] A. Baffezoli, E. Calo, *Compos. Sci. Technol.*, **2004**, 64: 839.
- [6] H. Baumann, M. Buehler, H. Fochem, F. Hirsinger, H. Zoblein, Falbe, *J. Angew. Chem., Int. Ed. Engl.*, **1988**, 27: 41.
- [7] U. Biermann, W. Friedt, S. Lang, W. Luhs, G. Machmuller, Metzger, M.R. Klaas, H.J. Schafer, Schneider, *Angew Chem., Int. Ed.* **2000**, 39: 2206.

- [8] J.H.P. Tyman, R.A. Johnson, M. Muir, R. Rokhgar, *J.Am.Oil Chem.Soc.*, **1989**, 66: 553.
- [9] D.D. Andjelkovic, R.C. Larock, *Biomacromolecules*, **2006**, 7: 927.
- [10] Tsujimoto, H. Uyama, S. Kobayashi, *Macromolecules* **2004**, 37: 177.
- [11] T. Eren, S.H. Kuşefoglu, *J. Appl. Polym. Sci.*, **2004**, 91: 2700.
- [12] H.John Crabtree, *ASAIO Journal*, **2003**, 49(3): 290-294.
- [13] M. Scheuer Leeser, W.Irnich., J.Kreuzer *PACE* ,**1983**, 6: 454.
- [14] J.W. Harthorne, *Int.J.Cardiol.*, **1984**, 6:423.
- [15] R..J. Zdrahala., *J.Bio.Mater. Appl.*, **1996**, 11: 37.
- [16] Z.S. Petrovic, A. Guo, I. Javni ,**2000**, U. S. Pat., 6,107,433.
- [17] H .Kluth, B. Gruber, B. Meffert, W. Huebner, **1988**,U S Pat., 4,-742,087.
- [18] R. Hoefler, B.Gruher, A.Meffert, R. Gruetzmacher, **1989**, U. S. Pat., 4,826,944.
- [19] K. I Suresh., V.S. Kishanprasad, *Ind. Eng. Chem. Res.*, **2005**, 44: 4504.
- [20] A .Guo, Y.J Cho, Z.S. Petrovic, *J. Polym. Sci., Part A: Polym.*, Chem. **2000**, 38: 3900.
- [21] A .Zlatanic, Z.S. Petrovic, K. Dusek, *Biomacromolecules*, **2002**, 3:1048.
- [22] Z. Wirpsza., Polyurethanes, Chemistry, Technology and Applications; Kemp, T. J., Ed.; Ellis Horwood PTR Prentice H.
- [23] J.D. Andrade, L.M Smith, D.E. Genois , Interfacial aspects of biomedical polymers, 1.Surface chemistry and physics,Plenum press,Newyork,USA,p.249,**1985**.
- [24] D. J. David, H.B. Staley Analytical Chemistry of Polyurethanes, Vol. XVI, Part III, High Polymers, p.365, **1974**,
- [25] P..J Flory , J. Rhener, *J.Chem. Phy.*, **1943**,11:521.
- [26] H.Hiaw, Z.H Ping, J.W Xie , T.Y Yu, *J. Polym. Sci., Part A, Polym.Chem.*, **1990**,28, 585
- [27] A. Broido, **1969**, *J. Polym. Sci. 1969 Part A-2: Polymer Physics*, 7, 1761–1773.
- [28] F.Garbassi, M.Mora, E. Occhiello, Polymer surfaces, from physics to technology. Chichester: John Wiley & Sons. **1998**.
- [29] V. Bharadwaj, K. Somani ,S. Kamsara **2002** *J.Macromol.Sci.,Pure Appl. Chem.*, A39 (1&2),115-27.
- [30] R. E. Lyon, *Polym.Degrad.Stab.*, **1998**, 61:201–210.