



## Effect of aliphatic diisocyanates on the properties of Cardanol-based polyurethanes

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### ABSTRACT

*New formulations of novel polyurethanes based on cardanol-formaldehyde resin, polypropylene glycol and two different aliphatic diisocyanates viz., hexamethylene diisocyanate(HDI) and isophorone diisocyanate(IPDI) are reported. Cardanol based novolac type phenolic resin has been condensed with hexamethylene diisocyanate/ isophorone diisocyanate to produce rigid polyurethanes. Tough polyurethanes have been produced by condensing the commercially available polyol, polypropylene glycol-1200(PPG-1200) with the above system. The physico-chemical, mechanical and thermal properties of polyurethanes have been studied. These studies revealed better mechanical properties and higher thermal stability of rigid polyurethanes and also the high performance character of the isophorone diisocyanate based polyurethanes with respect to their mechanical and thermal properties when compared with those of the hexamethylene diisocyanate -based polyurethanes.*

**Keywords:** cardanol, hexamethylene diisocyanate, isophorone diisocyanate, polypropylene glycol-1200, rigid polyurethane, tough polyurethane.

### INTRODUCTION

Innovative technologies and competitive industrial products are reducing the dependence on petrochemicals for the productions of polymers. Increasing concern about the deteriorating environment caused by conventional polymers directed worldwide research of both academic and industrial laboratories towards the renewable resources [1–5]. Vegetable oils are one of the most readily available alternative renewable resources. Among the renewable resources, cashew nut shell liquid (CNSL), an agricultural renewable resource material obtained as a byproduct of the cashew industry is unique in that it contains a natural phenolic distillate, cardanol[6]. The functional group in it can be activated for the preparation of many speciality materials, such as liquid crystalline polyesters [7], nanotubes [8], cross-linkable polyphenols [9] and polyurethanes [10-14]. Polyurethanes are very large and varied family of incredible, versatile and useful engineering material. They are produced by the reaction between diols and diisocyanates. Thus polyurethanes provide a versatile range of properties and find extensive applications as fibers

and films [15], paints and lacquers [16], adhesives [17-18], foam [19-20] and elastomers[21-22] especially in the biomedical field. 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. Thus the ultimate properties of the urethane can be varied through the wide range by employing different isocyanate curatives.

In the present communication, a detailed study of the synthesis of -NCO terminated polyurethane and the influence of two different of aliphatic diisocyanate viz. hexamethylene diisocyanate(HDI) and isophorone diisocyanate (IPDI), on the properties of the polyurethanes are reported. Cardanol is made to react with formaldehyde in the mole ratio 1:0.7 in the presence of a dicarboxylic acid catalyst, sebacic acid to form cardanol - formaldehyde resin. The resulting methylolated cardanol-formaldehyde resin is allowed to condense with hexamethylene diisocyanate (HDI)/ isophorone diisocyanate (IPDI) to give the rigid polyurethanes. Commercially available polyol such as polypropylene glycol-1200 (PPG-1200) is also condensed with the same diisocyanates to get the tough polyurethanes.

## MATERIALS AND METHODS

### Experimental

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, epichlorohydrin and hexamethylene diisocyanate (HDI) were received from M/s E. Merck, Germany. Polypropylene glycol-1200 (PPG-1200) was received from Aldrich Chemicals (USA). Isophorone diisocyanate (IPDI) and the catalyst dibutyltin dilaurate (DBTDL) were received from Fluka Chemie (UK). The chemicals were used as received.

<sup>1</sup>H-NMR spectra of the synthesized resins were recorded using the R 248×H×Hitachi 300 MHz NMR spectrometer. Infrared spectra were recorded in a JASCO FT-IR spectrometer by KBr pellet method. Specific gravity, iodine value, hydroxyl value and intrinsic viscosity of the resins were determined according to the IS standard 840-1964. Molecular weight of the resins were determined by gel permeation chromatography using  $\mu$ -styragel columns, 100 Å and 500 Å, UV detector and 280 nm filter. Crosslink density of the polyurethane was found out by conducting swelling experiment. The swelling measurements of the polyurethanes have been carried out in solvents having different solubility parameters. From the swelling coefficient of polyurethanes, the crosslink density was determined using modified Flory - Rehner equation [23]. Indentation hardness (shore-A) was determined as per ASTM standard D2240 using durometer. Tensile strength of the polyurethanes was determined as per ASTM standard D412. 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.

### Synthesis of cardanol-formaldehyde resin

The monoene constituent of cardanol has been separated by argentation liquid chromatography method [24]. High ortho multinuclear cardanol - formaldehyde resin (C-F) 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 was added to the cardanol through a dropping funnel. The reaction was carried out at temperature 120 ± 5°C for 3 hours and then at 150 ± 5°C for 2 hours. The initial pH value of the mixture was lowered from 5 to 3 after 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 and analyzed.

### Synthesis of rigid polyurethanes

Rigid polyurethane sheets (HPU-R and IPU-R ) were prepared by treating the vacuum- dried cardanol-formaldehyde resin with hexamethylene diisocyanate(HDI)/isophorone diisocyanate (IPDI) keeping the isocyanate index (NCO/OH mole ratio) constant at 1.4. The novolac resin, hexamethylene diisocyanate and the catalyst dibutyltin dilaurate were mixed well physically in a small plastic cup at room temperature and poured into a flat iron mould .The polyurethane sheets formed were allowed to stand for 24 hours, demoulded and cured in a vacuum oven at 80°C for 48 hours .

### Synthesis of tough polyurethanes

Tough polyurethane sheets (HPU-S and IPU-S) were prepared by mixing the vacuum-dried cardanol- formaldehyde resin, hexamethylene diisocyanate (HDI)/ isophorone diisocyanate (IPDI) and commercially available polypropylene glycol-1200 (PPG-1200) at room temperature keeping the isocyanate index (NCO/OH mole ratio) constant at 1.4. The reaction condition and the curing process were carried out in the same way as indicated in the case of rigid polyurethanes.

## RESULTS AND DISCUSSION

### Spectral data

In the  $^1\text{H-NMR}$  spectra of cardanol- formaldehyde resin (Fig. 1), the peak at 6.60–7.20  $\delta$  is due to the aryl protons of benzene nuclei, the peak around the region 6.45  $\delta$  is due to the phenolic

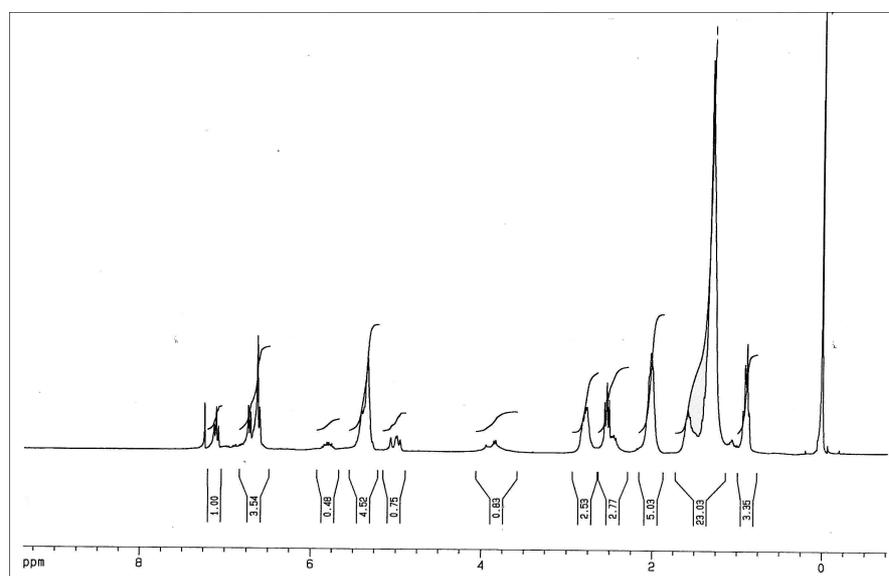
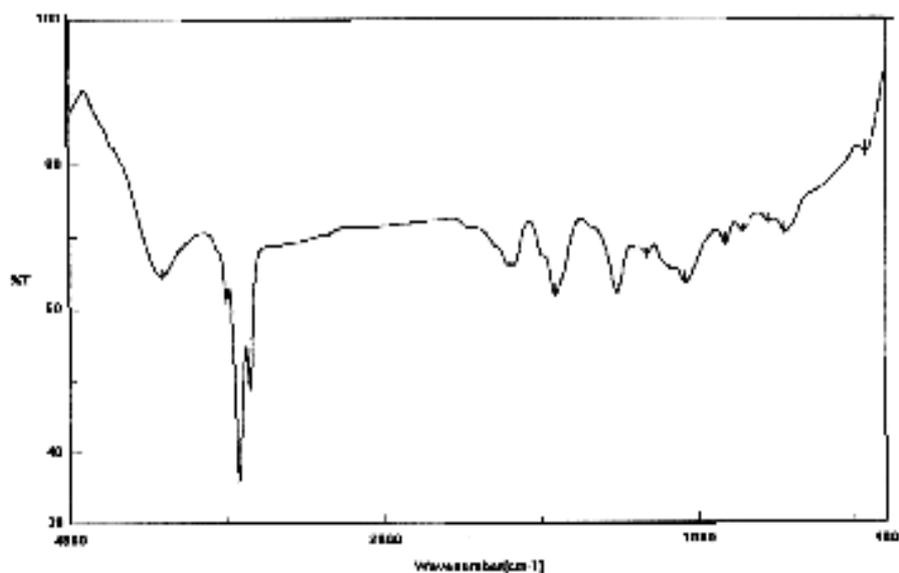


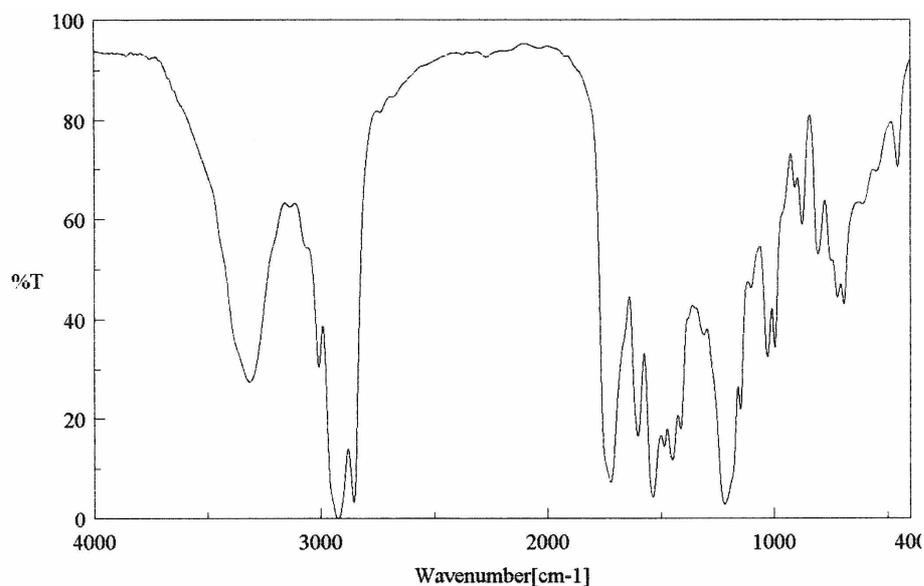
Figure 1:  $^1\text{H-NMR}$  spectrum of cardanol-formaldehyde resin

hydroxyl, the peak at 4.90–5.30  $\delta$  is due to methylene ( $\text{C}=\text{CH}_2$ ) proton of long alkyl side chain originally present in cardanol and the peak at 0.88–2.70  $\delta$  is due to the long aliphatic side chain. The small peak at 0.80  $\delta$  is due to terminal methyl group of the chain. The strong peak at 1.30  $\delta$  is attributed to the long chain of the side chain. The peak at 3.6  $\delta$  also indicates methylene proton of  $\text{C}_6\text{H}_5\text{-CH}_2\text{-C}_6\text{H}_5$  for the bridge between the phenyl rings. All these spectral data indicate that the condensation of methylolated cardanol has been completed under experimental condition.

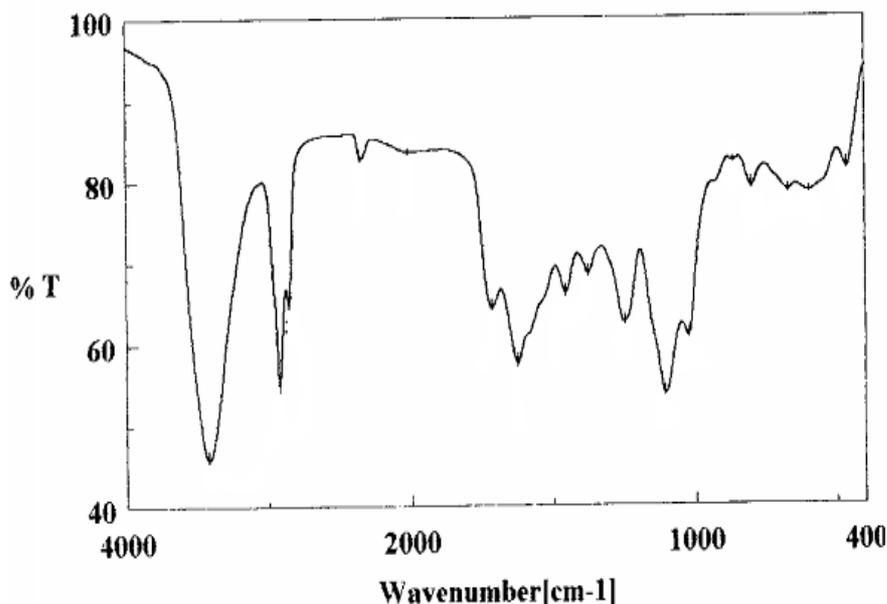


**Fig. 2: IR Spectrum of cardanol- formaldehyde resin**

In the case of IR spectral data of cardanol-formaldehyde resin (Fig.2), the peak at  $913\text{ cm}^{-1}$  is due to substitution in benzene nuclei and the peaks at  $773\text{ cm}^{-1}$  and  $697\text{ cm}^{-1}$  are due to three adjacent hydrogen atoms in the benzene nuclei. The peak at  $722\text{ cm}^{-1}$  indicate the ortho-substitution at benzene nuclei. In the present study, the condensation of cardanol with formaldehyde in the mole ratio (1:0.7) in the presence of sebacic acid leads to ortho- substituted product.



**Fig. 3: IR Spectrum of Rigid polyurethane**



**Fig. 4: IR Spectrum of Tough polyurethane**

The IR spectra of the rigid and tough polyurethanes (Fig. 3 – Fig. 4) showed characteristic absorption at  $3301\text{cm}^{-1}$  corresponding to urethane linkage (-NH stretching, bonded). The peaks at  $1718\text{cm}^{-1}$  corresponding to C=O stretching (free) in urethane,  $1645\text{cm}^{-1}$  corresponding to C=O stretching (bonded) in urethane and  $1537\text{cm}^{-1}$  corresponding to N-H bending in urethane.

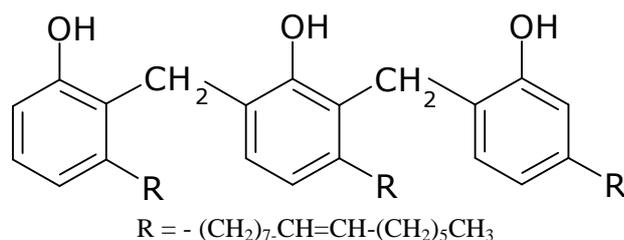
### Physico-chemical properties

Physico-chemical properties of the cardanol and the synthesized resins are presented in Table 1. From Table 1, it is clear that the parent resin possess mild phenolic odour. A slight decrease in the iodine value of the resin may be due to the steric hindrance of adjacent bulky groups to the addition of iodine monochloride. The specific gravity and intrinsic viscosity of the resins are found to be greater than that of cardanol.

**Table 1: Physico-chemical properties of cardanol and C-F resin**

S.No	Properties	cardanol	C-F resin
1.	Colour	Pale brown	Dark brown
2.	Odour	Mild phenolic	Mild phenolic
3.	Specific gravity(g/cc)at 30°C	0.9294	0.9340
4.	Intrinsic viscosity	0.0310	0.0314
5.	Iodine value	223	211.9
6.	Hydroxyl value (mg KOH/g)	182.00	155.3
7.	Molecular Weight	302	924
8.	Number of hydroxyl groups	1	3

The molecular weight determination, hydroxyl number and IR spectral analysis leads to predict the structure of cardanol-formaldehyde resin as (1).



### Swelling Characteristics of polyurethane

The hard segment percentage and the crosslink densities of the synthesized polyurethanes were presented in Table 2. The swelling characteristic of polyurethanes is depicted in Fig. 5. In the present investigation, the crosslink density of rigid polyurethanes is found to be higher in comparison with those prepared with the addition of commercial polyol, PPG-1200. Accordingly the molecular weight between crosslinks,  $M_c$  is also found to be minimum in these cases. This may be due to the fact that rigid polyurethanes possess 100% hard segment whereas the percentage of hard segments in the commercial polyol-added polyurethanes is found to be only 60%. The low crosslink density of commercial polyol-added polyurethanes may be due to the steric hindrance of the pendant methyl groups of polypropylene glycol.

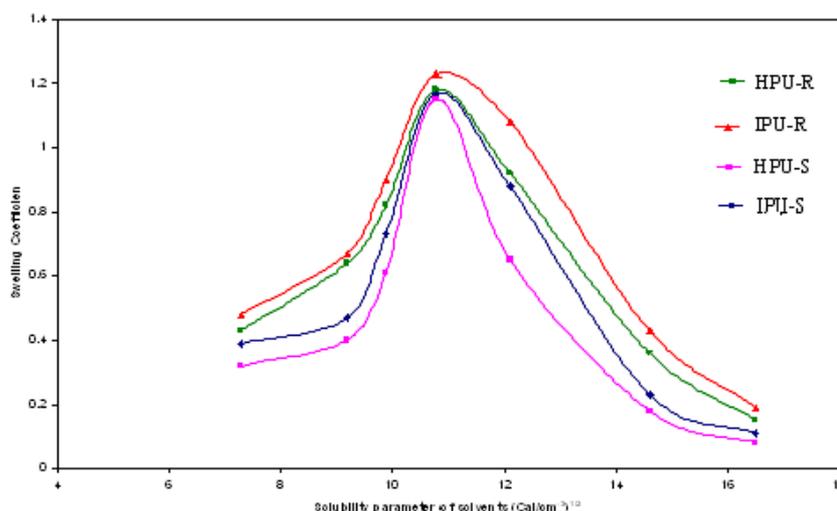


Fig. 5: Swelling Coefficient curves of polyurethanes

Table 2: Swelling characteristic data of polyurethanes

Polyurethane	% Hard segment	Swelling coefficient Q	Crosslink density ( $\times 10^{-3}$ )	Molecular weight between cross links ( $\text{mole}^{-1}$ )
HPU-R	100	1.22	1.006	994
HPU-S	60	1.46	0.944	1060
IPU-R	100	1.25	0.997	1003
IPU-S	60	1.62	0.947	1056

### Mechanical properties of polyurethanes

Properties such as Shore A hardness, tensile strength and percentage elongation, are furnished in Table 3. The shore A hardness of the rigid polyurethanes are found to be higher than those of tough polyurethanes. The tensile test data shows that the rigid polyurethanes (HPU-R and IPU-R) crumble during tensile test. This is attributed to the higher crosslink density of the rigid polyurethanes.

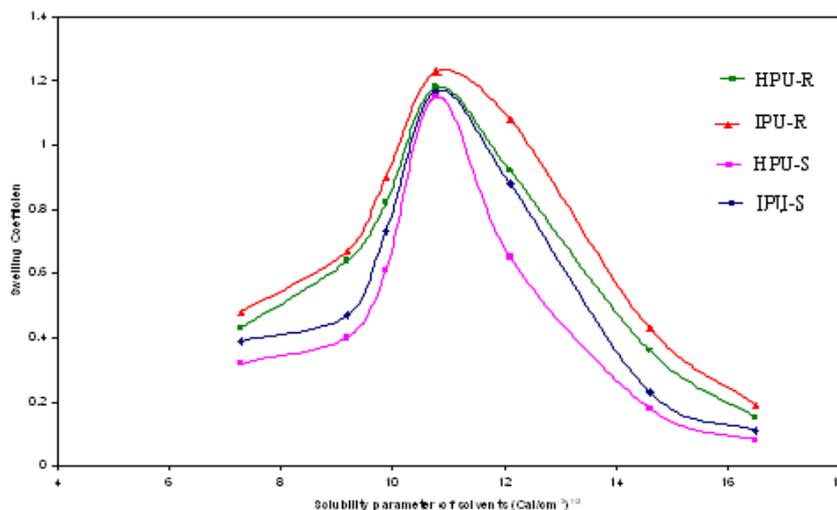
**Table 3: Mechanical properties of polyurethanes**

Polyurethane	Hardness Shore-A	Crosslink density ( $\times 10^{-3}$ )	Tensile strength (Mpa)	Elongation (%)
<b>HPU-R</b>	<b>88</b>	<b>1.006</b>	<b>Brittle</b>	<b>Brittle</b>
HPU-S	68	0.944	13.1	159
<b>IPU-R</b>	<b>85</b>	<b>0.997</b>	<b>Brittle</b>	<b>Brittle</b>
IPU-S	78	0.947	23.6	139

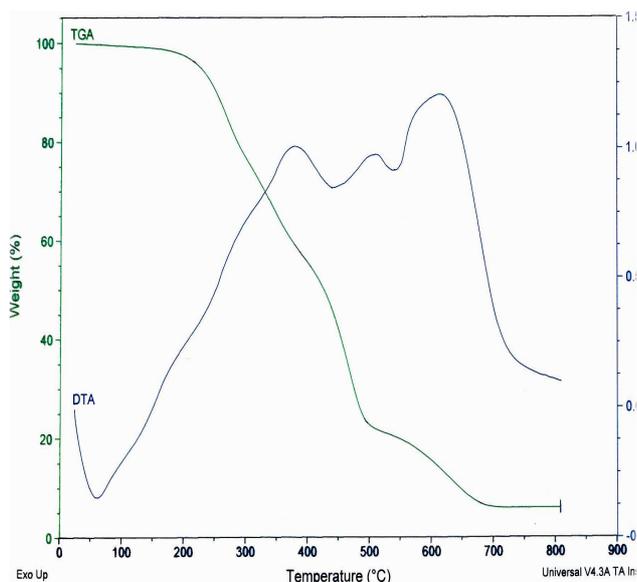
Increase in elongation in tough polyurethanes is due to the flexibility of the chain introduced due to the addition of the commercial polyol PPG-1200 along with the diisocyanates and resin. It is also noticed that the polyurethanes based on IPDI are found to possess better mechanical properties than those of the HDI- based polyurethanes. This may be due to the fact that the aliphatic HDI has flexible and symmetric open chain structure with two primary isocyanate groups whereas the cyclo- aliphatic IPDI is has a sluggish unsymmetric structure in which one of the isocyanate groups is secondary in nature. Thus IPDI with its rigid and bulky structure increases the tensile strength by interchain steric hindrance of the molecular slippage as it has been reported earlier [25].

### Thermal properties of polyurethanes

In the present study, DTA and TGA thermograms of cured rigid polyurethanes (HPU-R, IPU-R) and tough polyurethanes (HPU-S, IPU-S) are presented in (Fig.5 – Fig.8) and the results are presented in Table 4 and Table 5.

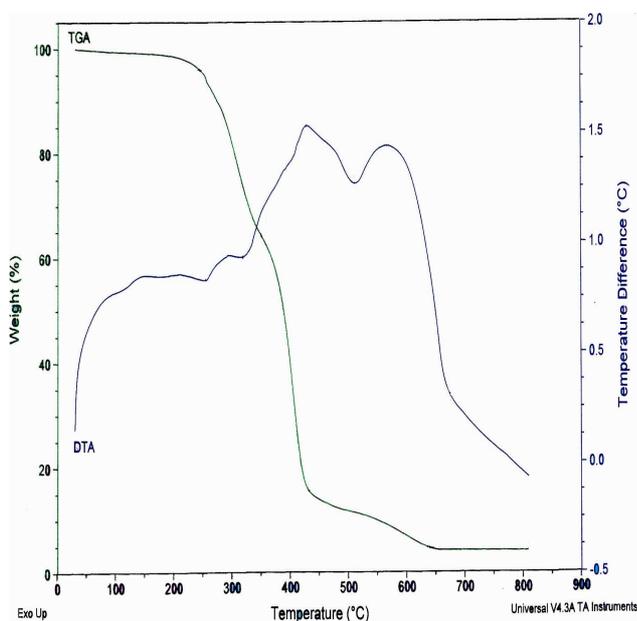
**Fig. 5 TGA and DTA curves of HPU- R****Table 4: DTA data of rigid and tough polyurethanes**

Polyurethane	Exotherm (°C)		
	First	Second	Third
<b>HPU-R</b>	<b>379</b>	<b>510</b>	<b>620</b>
HPU-S	300	428	568
<b>IPU-R</b>	<b>373</b>	<b>471</b>	<b>625</b>
IPU-S	399	480	587

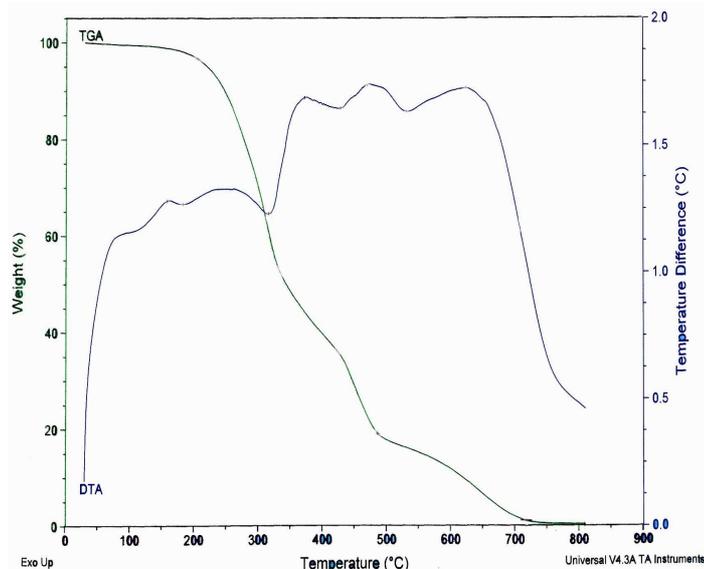


**Fig. 6 TGA and DTA curves of HPU- S**

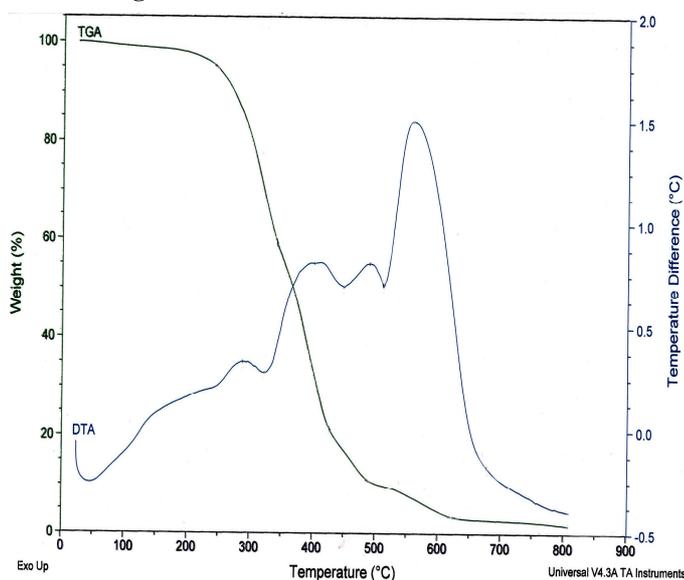
The DTA thermogram does not show any strong endothermic peak for softening. But three exotherms are invariably seen in all these polyurethanes. The first exotherm for rigid as well as the tough polyurethanes are relatively weak. This is attributed to the cleavage of long alkyl side chain of phenyl ring and also due to the cleavage of allophanate linkages at low temperature. However the second and the third exotherms for the polyurethanes are strong. All the three exotherms of the rigid polyurethane occur at higher temperature and thus possess higher degradation temperature in comparison with that of the tough polyurethane due to the higher crosslink density of the rigid polyurethane.



**Fig. 7: TGA and DTA curves of HPU-S**



**Fig. 8: TGA and DTA curves of IPU-R**



**Fig. 9: TGA and DTA curves of IPU-S**

**Table 5: TGA data of rigid and tough polyurethanes**

Polyurethane	% Weight loss at various temperatures °C				
	100	200	300	400	500
<b>HPU-R</b>	0	0.5	15	<b>35</b>	<b>85</b>
HPU-S	0	3	15	46	90
<b>IPU-R</b>	0	2	15	<b>31</b>	<b>80</b>
IPU-S	0	0	10	44	86

TGA curves for decomposition of polyurethanes show two-stage decomposition. In the case of all the polyurethanes, a small % weight loss observed in the temperature range 50°C -150°C is apparently associated with adsorbed water. At higher temperatures (400° C and 500° C), the weight loss observed in the rigid polyurethanes are HPU-R (35%, 85%) and IPU-R (31%, 80%) respectively. The corresponding tough polyurethanes HPU-S and IPU-S showed higher

percentage of weight loss ( 46 %, 90 %) and (44%, 86%) respectively at the same temperature thereby proving the higher thermal stability of the rigid polyurethanes.

### CONCLUSION

From the results, it can be concluded that the polyurethanes based on IPDI were found to possess better mechanical property and higher thermal stability than those of the HDI- based polyurethanes. Among all the polyurethanes prepared, rigid polyurethanes were found to possess higher hardness when compared to the tough polyurethanes. Also rigid polyurethanes exhibit higher thermal stability than those of tough polyurethanes. The performance characters of the above polyurethanes also reflect the better mechanical property of the polyurethanes.

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