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Processability and Characteristics of Novel polyurethanes from Cardanol

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ABSTRACT

The development of a new class of polyurethanes from cardanol, a renewable organic resource obtained as a byproduct of the cashew industry, is reported. Cardanol based novolac type phenolic resin has been synthesized by condensing cardanol with formaldehyde in the mole ratio 1:1 using sebacic acid as catalyst. The resulting novolac resin has been subjected to epoxidation followed by hydrolysis to give the hydroxyalkylated derivative (synthesized polyol).The novolac resin/synthesized polyol has been condensed with hexamethylene diisocyanate to produce rigid polyurethanes. Tough polyurethanes have been produced by condensing novolac resin / synthesized polyol with the commercially available polyol, polypropylene glycol-1200(PPG-1200) and hexamethylene diisocyanate. The physico-chemical, mechanical and thermal properties of polyurethanes have been studied. These studies revealed the high performance character of rigid polyurethanes with respect to their mechanical and thermal properties.

Keywords: Cardanol, hexamethylene diisocyanate, polypropylene glycol-1200, rigid polyurethane, tough polyurethane. .

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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. 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].Considerable attention from polymer scientists is devoted to utilize their potential attributes as a substitute for petrochemical derivatives and has found use in cardanol-based phenolic resins for break lining, surface coatings, and other miscellaneous applications.[7,8]. Of late it has been used in the preparation of many speciality materials such as liquid crystalline polyesters[9], nanotubes [10],cross-linkable polyphenols[11]and polyurethanes[12-16]. Since the synthesis of polyurethanes by Bayer[17] in 1937,their utilisation has become ubiquitous. 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[19] ,pacemaker lead insulation[20], Polyurethanes vascular grafts[21]and artificial heart valves[22].

In the present study, cardanol is made to react with formaldehyde in the mole ratio 1:1 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, a nucleophilic compound (polyol) through epoxidation followed by hydrolysis.Such nucleophilic high molecular weight polyol is allowed to condense with hexamethylene diisocyanate (HDI) which can act as an electrophile to give the rigid polyurethane. Commercially available polyol such as polypropylene glycol-1200 (PPG-1200) is also condensed with the same diisocyanate along with the particular composition of the synthesized polyol to get the tough polyurethane.

MATERIALS

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) and the catalyst dibutyltin dilaurate (DBTDL) was received from Fluka Chemie(UK).The chemicals were used as received.

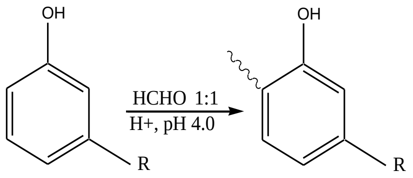
EXPERIMENTAL

^{1}H–NMR spectra was recorded using theR 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 μ-styragel columns, 100 Å and 500 Å, UV detector and 280 nm filter. Cross-link density of the polyurethane was found out by conducting swelling experiment. 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 and hydroxyalkylated resin

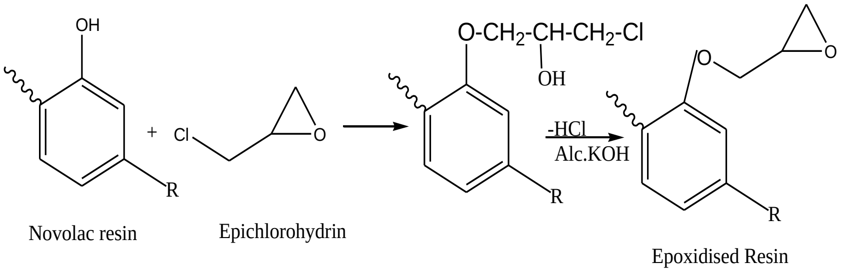
The monoene constituent of cardanol has been separated by argentation liquid chromatography method [23]. High ortho multinuclear cardanol - formaldehyde resin (LR) was synthesized using cardanol: formaldehyde in the mole ratio 1:1 using sebacic acid as catalyst. Cardanol was taken in a three necked round 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^{0}C for 3 hours and then at 150±5^{0}C for 2 hours. 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 and analyzed. The cardanol- formaldehyde resin was epoxidised using epichlorohydrin and the resulting epoxidised resin was hydrolysed with dilute hydrochloric acid. The hydroxyalkylated resin(LREH) thus formed was purified by washing with distilled water several times and then dried over vacuum at 60^{0}C. (Scheme 1)

Formylation of cardanol

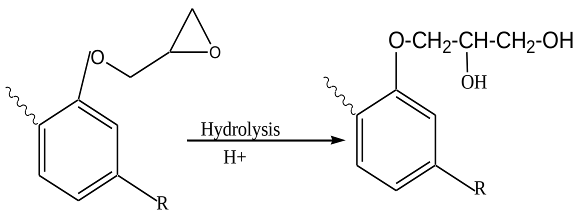


Novolac resin

Epoxidation of novolac resin



Formation of hydroxyalkylated resin



Hydroxyalkylated resin

Scheme 1

Synthesis of rigid polyurethanes

Rigid polyurethane sheets (LRH and LREHH) were prepared by treating the vacuum-dried cardanol formaldehyde resin/synthesized polyol with hexamethylene diisocyanate(HDI),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 80^0C for 48 hours .

Synthesis of tough polyurethanes

Tough polyurethane sheets(LRHP and LREHHP) were prepared by mixing the vacuum dried cardanol- formaldehyde resin/synthesized polyol, hexamethylene diisocyanate (HDI) and commercially available polypropylene glycol-1200 (PPG-1200) at room temperature keeping the isocyanate index (NCO/OH mole ratio) constant at1.4.The reaction condition and the curing process were carried out in the same way as indicated in the case of rigid polyurethanes.

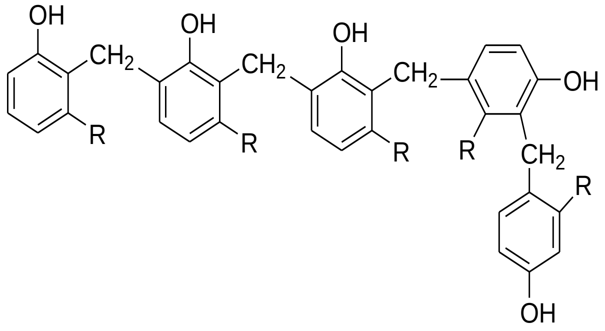
RESULTS AND DISCUSSION

Spectral Data

In the ^{1}H–NMR spectra of cardanol formaldehyde resin, the peak at 6.60–7.20 δ is due to aryl protons of benzene nuclei, the peak around the region 6.45 δ *is* due to the phenolic hydroxyl, the peak at 4.90–5.30 δ is due to methylene ($C=CH_2$) proton of long alkyl side chain originally present in cardanol and the peak at 0.88–2.70 δ *is* due to the long aliphatic side chain. The small peak at 0.80 δ *is* due to terminal methyl group of the chain. The strong peak at 1.30 δ *is* attributed to the long chain of the side chain.The peak at 3.6 δ also indicates methylene proton of $C_6H_5–CH_2– C_6H_5$ 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.1). In the case of IR spectral data of cardanol-formaldehyde resin, the peak at 913 cm^{-1} is due to substitution in benzene nuclei and the peaks at 773 cm^{-1} and 697 cm^{-1} are due to three adjacent hydrogen atoms in the benzene nuclei. The sharp peaks at 722 $cm^{-1}$and at 858 cm^{-1} indicate the ortho and para substitution repectively at benzene nuclei. (Fig. 2**)**.. In the present study, the condensation of cardanol with formaldehyde in the mole ratio(1:1) in the presence of sebacic acid leads to ortho-para substituted product . The IR spectra of the synthesized hard and soft polyurethanes showed the characteristic absorption at 3301cm^{-1} corresponding to urethane linkage(-NH stretching,bonded),1718cm^{-1} corresponding to C=O stretching (free) in urethane,1645cm^{-1} corresponding to C=O stretching (bonded) in urethane and 1537cm^{-1} corresponding to N-H bending in urethane (Fig. 3) and (Fig. 4).

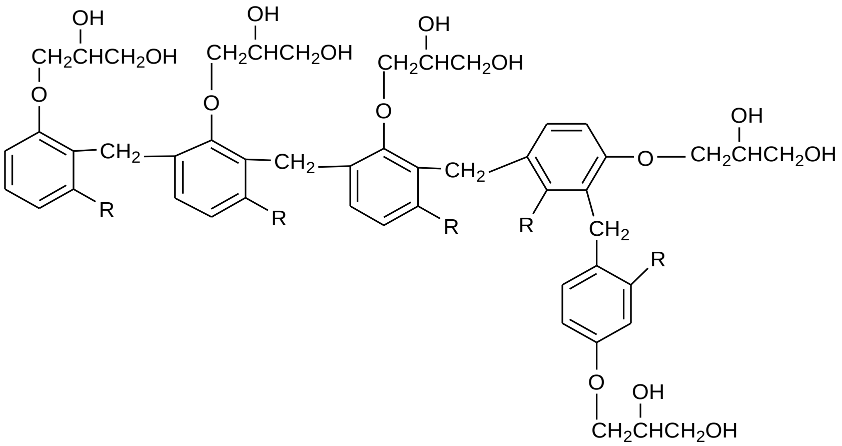
Physico-Chemical Properties

Physico-chemical properties of the cardanol and the synthesized resins are presented in (Table 1)**.** From the table, it is clear that both the parent resin and the polyol 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. However, iodine value of the polyol is not changed significantly indicating no change in the effect of steric hindrance offered by bulky groups to olefinic addition of iodine monochloride.. The specific gravity and intrinsic viscosity of the resins are found to be greater than that of cardanol. Compared to its parent resin, the polyol has higher specific gravity and hydroxyl number. Higher specific gravity of the polyol is due to intra- and inter-molecular hydrogen bonding through dihydroxypropyl units. The molecular weight determined by gel permeation chromatography also indicates the increase of molecular weight due to dihydroxypropyl units. The molecular weight determination, hydroxyl number and IR spectral analysis leads to predict the structures of cardanol-formaldehyde resin and the synthesized polyol as (1) and (2).



R - $-(CH_2)_7-CH=CH-(CH_2)_5CH_3$

(1)



(2)

Mechanical properties of polyurethanes

Properties such as shore A hardness, elongation at break (%), tensile strength are furnished in Table 2.. The shore A hardness and crosslink density of the rigid polyurethane is higher than that of the tough polyurethane.The tensile test data of the rigid polyurethane (LRH,LREHH) shows that the polyurethanes crumble during tensile test. This is attributed to the higher crosslink density of the rigid polyurethane. Increase in elongation in tough polyurethane is due to the flexibility of the chain introduced due to the addition of commercial polyol,(PPG-1200) along with resins LR and LREH.

Thermal properties of polyurethanes

In the present study, DTA and TGA thermograms of cured rigid polyurethanes (LRH,LREHH)and tough polyurethanes (LRHP,LREHHP) are presented in(Fig.5-Fig. 8) and the results are presented in Table 3 and Table 4 .The DTA thermogram does not show any endothermic peak for softening. The first exotherm of 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 as has been reported earlier .However the second and the third exotherms for the polyurethanes are strong. The exotherms of the rigid polyurethane occur at higher temperature and possess higher degradation temperature in comparison with that of the tough polyurethane due to the higher crosslink density of the rigid polyurethane. TGA curves for decomposition of polyurethanes show two-stage decomposition. In all the TGA curves,a small % weight loss is observed in the temperature range of
50˚ C -150˚ C ,which is apparently associated with adsorbed water.At higher temperature
(500˚ C), the weight loss in the rigid polyurethanes(85% and 80%) is found to be lesser than the corresponding tough polyurethanes(90% and 86%) thereby proving the higher thermal stability of the rigid polyurethanes.

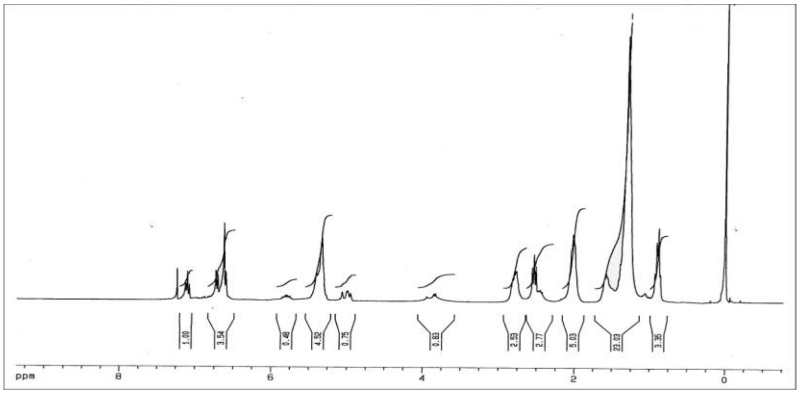


Fig. 1 ^{1}H–NMR Spectrum of cardanol-formaldehyde resin

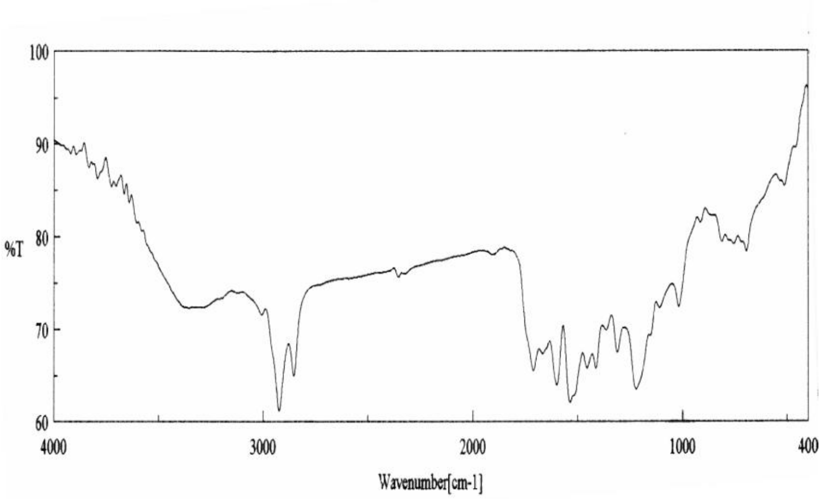


Fig. 2 IR Spectrum of cardanol-formaldehyde resin

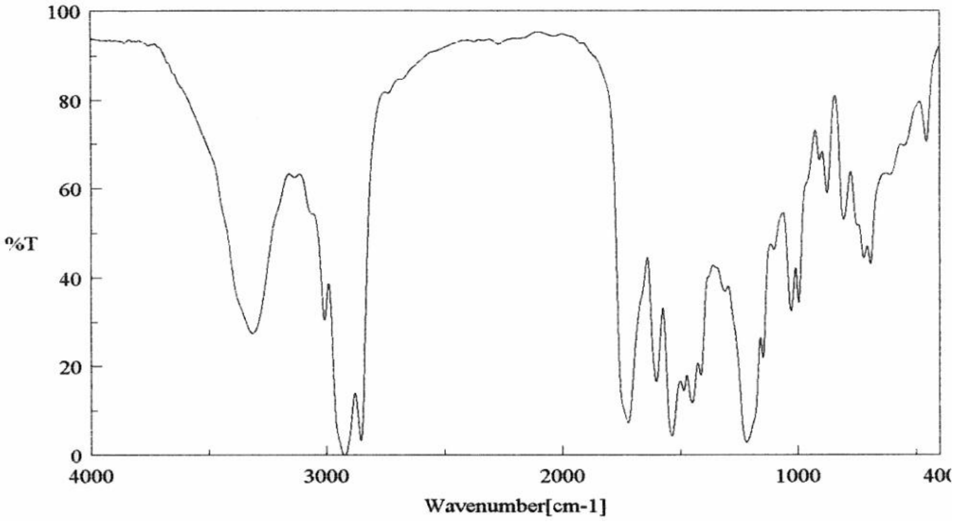


Fig. 3 IR Spectrum of rigid polyurethane

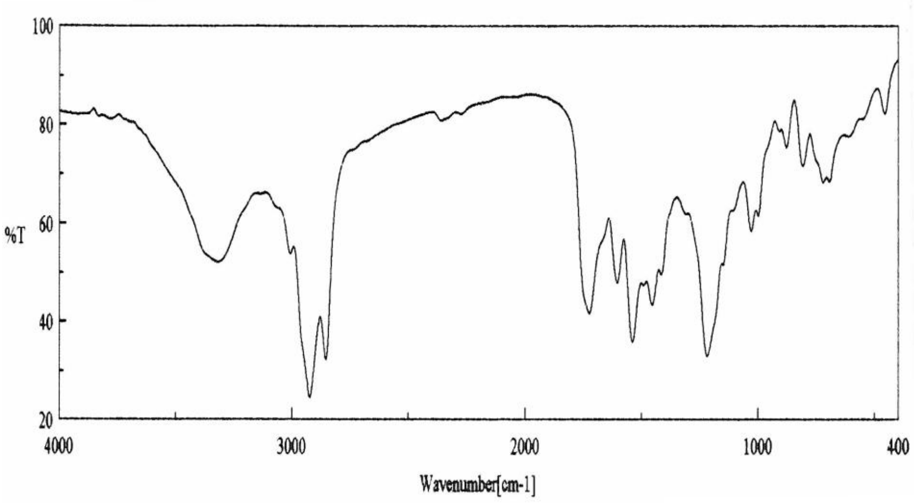


Fig. 4 IR Spectrum of tough polyurethane

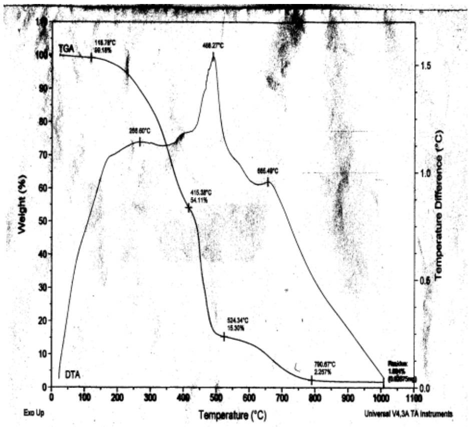


Fig. 5 TGA and DTA curves of LRH

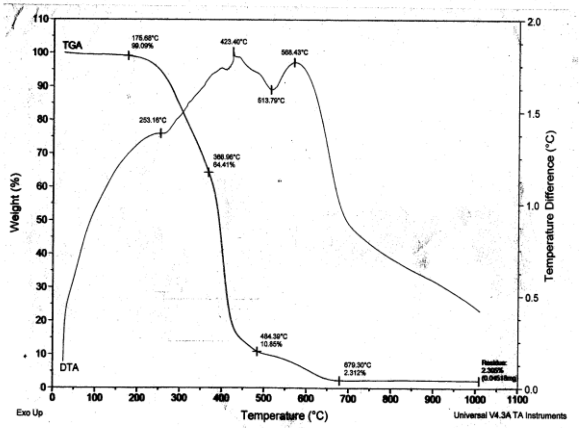


Fig. 6 TGA and DTA curves of LRHP

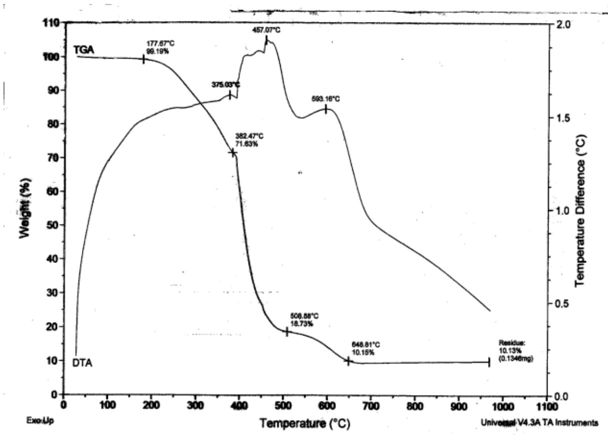


Fig.7 TGA and DTA curves of LREHH

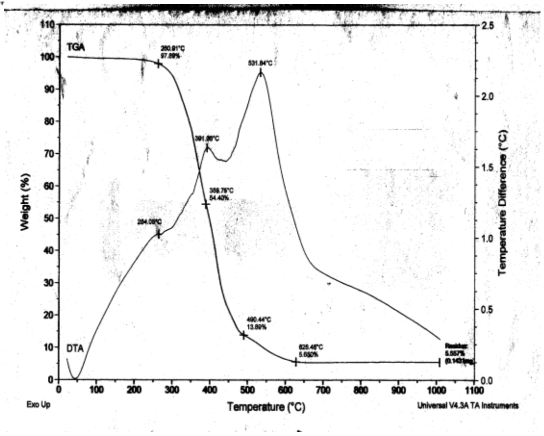


Fig.8 TGA and DTA curves of LREHHP

Table 1 Physico-Chemical properties of cardanol and the synthesized resins

S.No	Properties	cardanol	LR	LREH
1.	Colour	Pale brown	Dark brown	Dark brown
2.	Odour	Mild phenolic	Mild phenolic	Mild phenolic
3.	Specific gravity(g/cc)at 30^{o}C	0.9340	0.9403	0.9496
4.	Intrinsic viscosity	0.0310	0.0328	0.0394
5.	Iodine value	223.20	221.8	222.8
6.	Hydroxyl value (mg KOH/g)	182.00	162.2	243.2
7.	Molecular Weight	302	1620	1940
8.	Number of hydroxyl groups	1	5	10

Table 2 Mechanical properties of rigid and tough polyurethanes

Polyurethane	Hardness Shore A	Cross link density ($\times 10^{-3}$)	Tensile strength (mpa)	% Elongation at break
LRH	88	1.5152	Brittle	Brittle
LRHP	75	1.5080	16.2	28.5
LREHH	95	1.4768	Brittle	Brittle
LREHHP	71	1.3258	27.7	16.32

Table 3 Differential Thermal Analysis data of rigid and tough polyurethanes

Polyurethane	Exotherm (°C)		
	First	Second	Third
LRH	266	**488**	**655**
LRHP	253	423	568
LREHH	375	**457**	**593**
LREHHP	264	391	531

Table 4 Thermogravimetric Analysis data of rigid and tough polyurethanes

Polyurethane	**% Weight loss at various temperatures °C**				
	100	200	300	400	500
LRH	0	0.5	15	35	**85**
LRHP	0	3	15	44	90
LREHH	0	2	15	31	**80**
LREHHP	0	0	10	46	86

CONCLUSION

From the results presently discussed, it can be concluded that the rigid polyurethanes were found to possess higher hardness when compared to the tough polyurethanes. Also rigid polyurethanes exhibit higher thermal stability than the tough polyurethanes. The performance characters of the above polyurethanes also reflect the better mechanical and thermal stability. Based on the above characteristics the polyurethanes have a wide number of applications that include flexible coupling connectors, earth mover equipments and farm machineries and find an extensive use in the biomedical field for making artificial organs.

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