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Studies on ageing performance of some novel polyurethanes

S. Gopalakrishnan* and T. Linda Fernando

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

ABSTRACT

New formulations of novel polyurethanes based on cardanol-formaldehyde resins, commercial polypropylene glycols and two different aliphatic diisocyanates 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 polyols viz., polypropylene glycol-1200(PPG-1200) and polypropylene glycol-2000 (PPG-2000) with the above system. The ageing performance of the newly developed polyurethanes has been studied. These studies revealed better hydrolytic, chemical and environmental resistance of rigid polyurethanes and also the high performance character of the isophorone diisocyanate based polyurethanes with respect to their ageing conditions.

Keywords: cardanol, diisocyanate, polypropylene glycol, polyurethanes, ageing.

INTRODUCTION

Polyurethanes are a prominent class of polymers which are synthesized from various polyols, diisocyanates and chain extenders and they can be structurally manipulated to achieve a wide range of properties suitable for various applications [1]. Polyurethanes have been successfully used for many years in industrial sectors[2] such as automotive, electric and electronic equipment, sports and leisure, aeronautics and the aerospace industry, etc. particularly in the biomedical field[3] due to an excellent balance between mechanical performance (high flexibility), excellent chemical barrier behaviour, soft tact and biocompatibility. This success comes from the outstanding properties brought by polyurethane backbones such as high solvent and mechanical resistance (hardness/flexibility compromise), very good adhesion onto various substrates, fast film formation and excellent weathering resistance. The use of polyurethanes as

biomaterials has been exploited for various implants, including cardiovascular devices[4-6], artificial organs[7-8], artificial ducts[9], contraceptives[10], vascular graft[11] etc., where biostability of the polyurethane is of prime concern[12].

The biphasic nature of the polyurethane is due to the presence of hard and soft segment in the polymer structure. The hard segmented isocyanate portion of the polymer contributes to the hardness, physical properties and abrasion resistance while the polyol contributes to the soft segment and provides much of the chemical resistance. However, the polyurethanes have shown their susceptibility to degradation under the conditions of their performance. Poly (ester) urethanes and poly (ether) urethanes which are widely used for long term applications have been shown to degrade under hydrolytic [13] conditions and in oxidative [14] environment respectively. In addition, environmental stress cracking (ESC) of polyurethanes is also another important way of polyurethane degradation [15]. Both earlier data [16] and the results of more recent detailed studies on the mechanism of hydrolysis of standard polyurethanes[17] proved that not only the structure of soft (polyol) segments, but also the structure of diisocyanates used for polyurethane synthesis had significant effect on their hydrolytic stability.

Degradation can lead to significant changes in the polymer mechanical properties, surface chemistry and structure leading to malfunction. However the degradability of polyurethanes in biological environments has led to the development of studies on tissue engineering [18].

Ageing under outdoor exposure and end-use continuous exposure leads to loss of properties due to degradation of polymer. The more dominating routes of degradation are hydrolysis and oxidation induced by various chemical environments, dissolution by solvents and degradation induced by heat in air and vacuum. Microbial degradation of polymers may also take place. Therefore it is essential to evaluate the polymers under ageing conditions. Herein we report the synthesis and ageing behaviour of the newly synthesized rigid and tough polyurethanes based on cardanol-formaldehyde resins.

EXPERIMENTAL SECTION

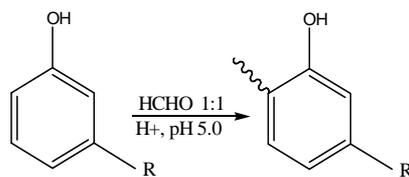
Materials

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 was 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 Na_2SO_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.

Synthesis of cardanol-formaldehyde resin

High ortho multinuclear cardanol - formaldehyde resin (R_1) 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 (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 (Scheme 1).



Novolac resin

Scheme 1 Formylation of cardanol

Synthesis of polyurethanes

The polyurethanes were synthesized in the form of thin sheets by transfer moulding technique. The rigid polyurethane sheets HPU-1 and IPU-1 were prepared using the novolac resin, hexamethylene diisocyanate/isophorone diisocyanate and the catalyst dibutyltin dilaurate (0.1% wt. of total charge). 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 reaction was carried out at room temperature in the case of hexamethylene diisocyanate, whereas the reaction mixture was heated to 75°C while using isophorone diisocyanate. The polyurethane sheets formed were allowed to stand for 24h, demoulded and cured in a vacuum oven at 110°C for 48h. Tough polyurethanes HPU-2, IPU-2, HPU-3 and IPU-3 were prepared by blending the vacuum dried cardanol-formaldehyde resin, hexamethylene diisocyanate/isophorone diisocyanate and the commercially available polyols, polypropylene glycol-1200 and polypropylene glycol-2000 respectively. The reaction condition and the curing process were carried out in the same way as indicated in the case of rigid polyurethanes. In both the cases, the isocyanate index was fixed as 1.4.

Ageing performance of polyurethanes

The studies on the stability of polyurethanes under various ageing conditions were carried out using the general guidelines of ASTM standards. The stability of the polyurethane was determined from the weight loss estimation. The ageing characteristics of both the rigid and tough segment polyurethanes of novolac resins were carried out using neat polyurethane sheets of dimensions 3 x 1 x 0.1 cm conditioned at 25° ± 1°C and 50 ± 5% relative humidity for 24 h. 100 ml of the medium was used in the hydrolytic stability and chemical resistance test. Five specimens were used for each test and average value was determined. The loss of weight was determined after vacuum drying the exposed sample. The maximum standard deviation for the average value was 5%. An electronic balance having an accuracy of 0.001g was used.

Hydrolytic stability test

Hydrolytic stability test for the polyurethanes was carried out according to ASTM D 3137. The weight loss of the polyurethanes on the media such as water, ethanol and salt solution (1N sodium chloride) was estimated by immersing the samples for the total period of 60 days under ambient conditions. The medium was changed and fresh medium was added at the interval of one week. The weight loss was determined.

Chemical resistance test

Polyurethanes are widely used in medical devices due to their broad property range, processing flexibility and biocompatibility. Increasingly, these devices are subjected to longer duration use, and exposed to a wide variety of chemically active agents. Chemical resistance test for the

polyurethanes was carried out according to ASTM C 267. The degradation of polyurethanes in dilute hydrochloric acid (1N), sodium hydroxide (1N) and 30% hydrogen peroxide were studied. The weight loss was determined.

Stability of polyurethanes in organic solvents

Stability of polyurethanes was determined in organic solvents such as dimethyl acetamide, diethyl ether and toluene at room temperature according to ASTM C 267. The conditioned samples were immersed in 100 ml of the organic solvent in an air-tight-container for the period of 60 days. The medium was changed once in a week. The weight loss was determined.

Dimensional stability test

Dimensional stability test was carried out according to ASTM D 1042. Samples with accurate dimensions were kept in an air oven at 70°C for a period of 60 days. After this period, the samples were cooled to room temperature and their dimensions were measured.

Stability under low temperature ageing

The stability of polyurethanes under low temperature ageing was carried out according to ASTM D 756. The change of hardness induced by low temperature ageing under the refrigeration storage conditions was determined. Polyurethane samples after conditioning were subjected to shore-A hardness testing. The samples were then kept in the low temperature cabinet at 4°C for a period of 60 days. The samples were removed, conditioned and tested for shore-A hardness.

Thermal stability (weight loss) under high temperature

The thermal stability of polyurethanes at high temperature was determined according to ASTM D 756. The conditioned samples were kept at 70° ± 2°C in an air oven for 60 days. After 60 days, the samples were removed from the oven, cooled to ambient temperature and weighed. The percentage weight loss and changes of hardness were determined.

Thermo-vacuum stability

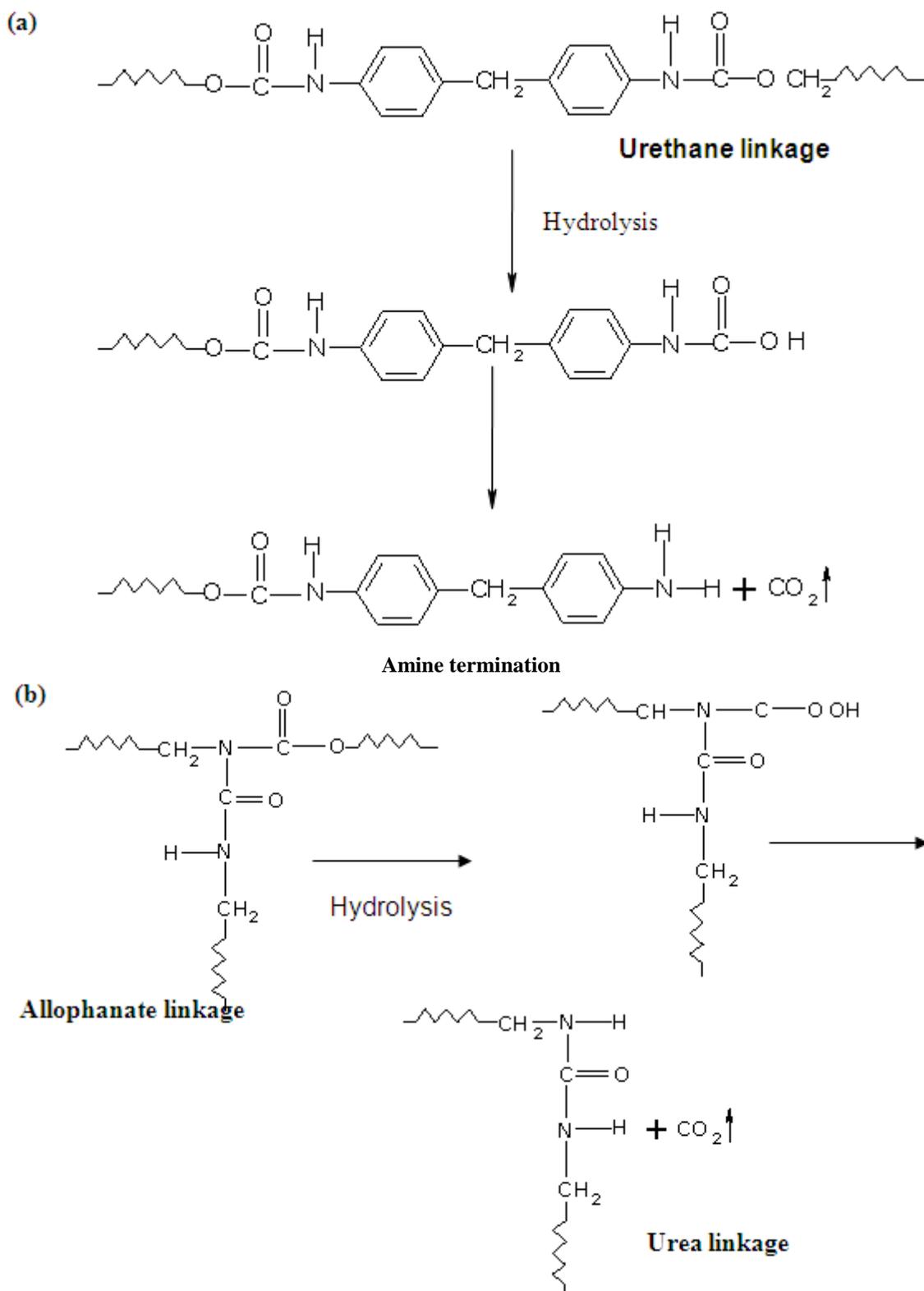
The stability of polyurethanes under thermo-vacuum ageing was determined according to ASTM D 756. The conditioned samples after determining Shore-A hardness were kept at 70° ± 2°C in a vacuum oven at 0 mm Hg for 60 days. The samples were removed from the vacuum oven after 60 days and cooled to ambient temperature. Shore-A hardness and loss of weight were determined.

Test for biodegradability

The environmental resistance of the synthesized polyurethanes was carried out using soil burial test [19-20]. The samples were buried in the soil for sixty days. The samples were removed from the soil once in 15 days to access the changes in their weight loss, mechanical strength and surface damage if any.

RESULTS AND DISCUSSION

The synthesized rigid polyurethanes are composed of a variety of groups in the polymer chain, including urethane, allophanate, hydrocarbon chain, and aromatic ring in addition to unreacted hydroxyl groups, whereas the tough polyurethanes contain ether units in addition to the above groups. The performance of these polyurethanes under ageing conditions largely depends upon this macromolecular architecture.



Scheme 1. Hydrolytic degradation in polyurethane

Evaluation of hydrolytic stability

In polyurethanes, the urethane or carbamate linkages are susceptible to hydrolysis similar to that of an ester linkage of a substituted carbamic acid. Unlike in the hydrolytic degradation of carboxylic ester linkage, the hydrolytic degradation occurs less readily in urethane groups [12]. The main hydrolytic attack [21] on polyester polyol based polyurethane is centered on ester and

urethane group. Some investigators also observed the hydrolytic degradation of polyurethanes based on polyol [22-25].

The hydrolytic attack on polyether polyol-based polyurethane is centered mainly on urethane group. Allophanate group in polyurethanes also undergoes hydrolytic degradation [26]. The hydrolysis at urethane linkage leads to amine termination. The hydrolysis at allophanate linkage leads to the formation of urea-linkage. The hydrolytic degradation takes place according to the schemes 1a and 1b presented below. The weight loss of the present polyurethane samples aged in water, methanol and sodium chloride solution (1N) are presented in Table 1. All the media exerted a similar influence on the hydrolytic degradation. Since the ionic permeation in the polyurethane matrix is very less, the effect of Na⁺, Cl⁻ ions on the degradation is less [27].

Table 1 Weight loss of polyurethanes in hydrolytic conditions

Polyurethane	Weight loss %		
	Water	Ethanol	Salt solution (in NaCl)
HPU	0	0	0
HPU-1	0.10	0.13	0.11
HPU-2	0.07	0.09	0.09
IPU	0	0	0
IPU-1	0.05	0.04	0.05
IPU-2	0.06	0.03	0.04

There is no weight loss in any of the newly synthesized rigid polyurethanes. However, a small weight loss was observed in the case of all the tough polyurethanes in all the three media. This is attributed to the presence of ether linkages in polyether urethane soft segments which render them particularly susceptible to physical and chemical attacks and also due to the higher hydrophilicity and water absorption character of the polypropylene glycol [28-29]. Among the tough polyurethanes, high degree of hydrolytic degradation is observed in the HDI treated polyurethanes in comparison with that of IPDI treated polyurethanes. This is attributed to the lower crosslink density of the flexible structured HDI.

Evaluation of stability in hostile chemical environment

The hostile reactive chemical environment such as acid, base and oxidizing agent also induces degradation of polyurethanes. Dilute acids and bases induce hydrolytic attack on polyurethanes.

Table 2 Weight loss of polyurethanes in hostile chemical environment

Polyurethane	Weight Loss (%)		
	Acid (1N HCl)	Base (1N NaOH)	Oxidant (30% H ₂ O ₂)
HPU	0.00	0.00	0.00
HPU-1	0.44	0.43	1.00
HPU-2	0.53	0.52	1.20
IPU	0.00	0.00	0.00
IPU-1	0.14	0.21	0.31
IPU-2	0.17	0.22	0.33

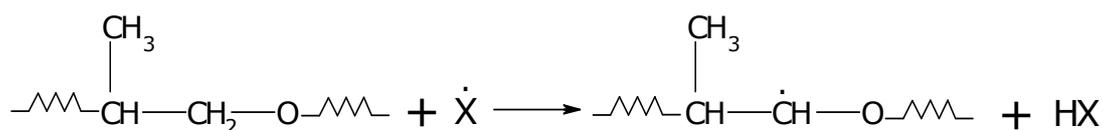
Oxidising agent induces oxidation of polyurethanes. Acid and base induced hydrolysis is similar to water induced hydrolysis, though the magnitude of hydrolytic degradation is larger in the case of former. The weight loss of polyurethanes is presented in Table 2.

In the present investigation, it has been found that the rigid polyurethanes are stable towards acid, base and oxidant. In the case of tough polyurethanes obtained by the addition of commercial polyols, in acid and alkali media, there is a slight percentage of degradation ranging from 0.43 – 0.53 and 0.14 - 0.22 for HDI and IPDI treated polyurethanes respectively. In the case of oxidant the weight loss percentage ranges from 1.00 – 1.20 and 0.31-0.33 for HDI and IPDI treated polyurethanes respectively. The increased stability of IPDI treated polyurethanes is due its high crosslink density resulting from the unsymmetrical structure of isophorone diisocyanate.

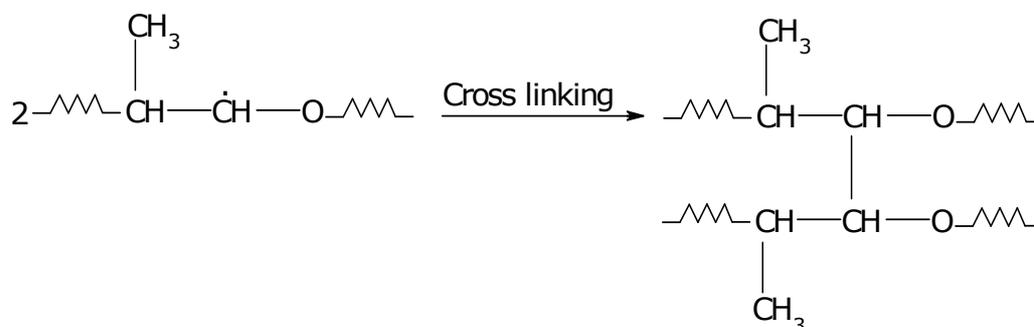
In acid and alkali media, the percentage weight loss is found to be in the ranges 0.14-0.43 and 0.17-1.2 for PPG-1200 and PPG-2000 added polyurethanes respectively. In the case of oxidant, the weight loss percentage ranges from 0.31– 1.1 and 0.33-1.21 for PPG-1200 and PPG-2000 added polyurethanes respectively. The decreased stability of PPG-2000 added polyurethanes may be attributed to the fact that, as the chain length of highly flexible PPG increases, the distance between two crosslinks increases leading to less dense crosslinked structure as reported elsewhere[30].The hydrolytic degradation in polyurethanes has already been presented in Scheme 1.

The hydrolytic degradation of the tough polyurethanes on exposure to the hostile chemical environment may be attributed to the increased hydrolytic potential of hydronium ions. In the case of base, the abstraction of hydrogen by hydroxyl group of the base leads to hydrolysis of polyurethanes. The oxidation of polyurethanes largely occurs with ether group of polyurethane [31-32].In the case of the tough polyurethanes, the concentration of ether group is found to be relatively higher than those of rigid polyurethanes. Hence degradation is more pronounced in tough polyurethanes leading to weight loss (Table 3). The oxidation of polyether polyol based polyurethanes is mediated by abstraction of labile hydrogen on the carbon alpha to the ether oxygen of polyether segment (Scheme 2).

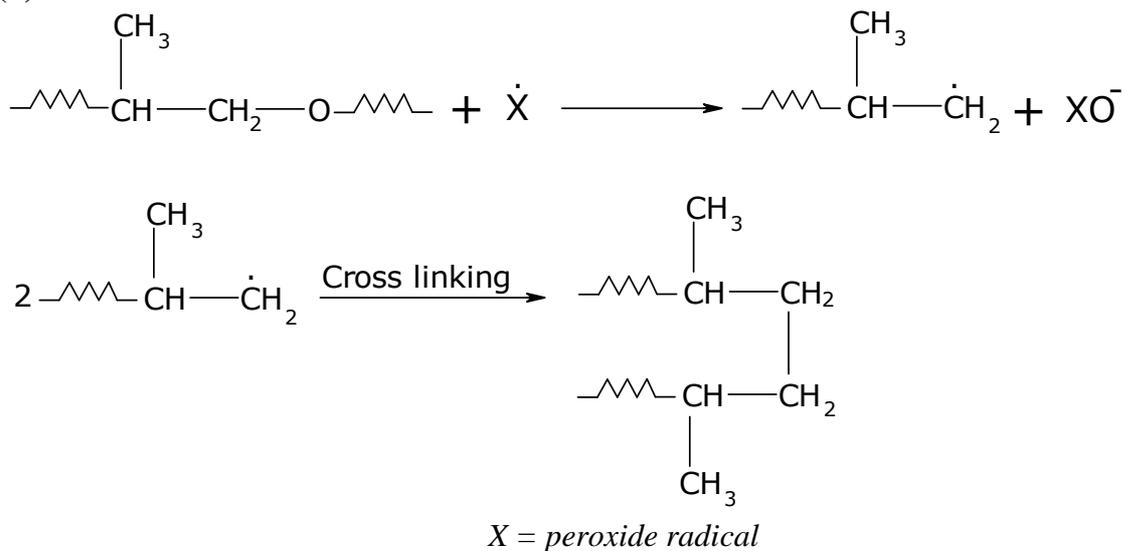
(a)



Polyol segment in polyurethane



(b)



Scheme 2. Oxidative degradation of polyurethane in hostile chemical environment

However another possible route of oxidation could be cleavage of C-O bond forming methylene terminated radical followed by cross linking as shown in Scheme 2 b. The mild degradation observed in the tough polyurethanes may be due to the advantageous aspect of cross linked structure of these polyurethanes.

Evaluation of stability in organic solvents

The non reactive chemical environment influences the stability of polyurethanes by solvation and dissolution of polymers. Aromatic organic solvent like toluene which is compatible for dissolution of phenol-formaldehyde resins and aliphatic organic solvent like dimethyl acetamide which is compatible for the dissolution of polyurethanes is selected for the present work. In addition to these two organic solvents, the commonly used organic solvent *viz* diethyl ether is also used in the present study. The solvents toluene and dimethyl acetamide were found to affect the tough polyurethanes. However, diethyl ether is found to be inert causing no weight loss in both the HDI and IPDI treated rigid and tough polyurethanes. All the polyurethanes are found to swell in dimethyl acetamide. DMA is found to penetrate into the polyurethane matrix and causes increase in weight. The degree of swelling varies with degree of crosslink density. However, there is no weight loss in rigid polyurethanes. Even the mild swelling was not observed in the case of toluene solvent. However, very small weight loss was noticed in polypropylene glycol-based polyurethanes. The weight loss of polyurethanes based on cardanol- formaldehyde resins are presented in Table 3.

In toluene, the percentage weight loss for both HDI and IPDI treated tough polyurethanes fall in the ranges 1.10 -1.23 and 0.96 -1.21 respectively . Thus the IPDI treated polyurethanes exert more chemical resistance than those of HDI treated ones. In a given mole ratio, the PPG-1200 added polyurethanes are found to be more stable than the PPG-2000 added analogues, due to the difference in their crosslink density as discussed in the previous section.

Table 3 Weight loss of polyurethanes in organic solvents

Polyurethane	Increase in weight in DMA	Weight Loss (%)	
		Diethyl ether	Toluene
HPU	66.29	0	0
HPU-1	73.74	0	1.10
HPU-2	74.91	0	1.23
IPU	65.26	0	0
IPU-1	66.10	0	0.96
IPU-2	65.99	0	1.21

Evaluation of dimensional changes under thermal ageing

Dimensional stability and thermal stability during hot environmental conditions are important for any end product for satisfactory functioning for intended duration of use. Dimensional changes under ageing condition can occur in any polymer either due to incomplete curing of the polymer or due to surface degradation induced by heat, ultraviolet light, and outdoor weathering [33].

Table 4 Dimensional changes in polyurethanes under thermal ageing

Polyurethane	Dimensional changes %		
	Length	Breadth	Thickness
HPU	0	0	0
HPU-1	0	0	0.65
HPU-2	0	0	0.69
IPU	0	0	0
IPU-1	0	0	0.51
IPU-2	0	0	0.54

Dimensional changes of cured polymer under thermal ageing conditions take place due to thermal oxidation. Even though there is no dimensional change in the length and breadth in all the polyurethanes, small decrease in thickness was noticed in the case of HDI and IPDI treated soft segment polyurethanes. The change in thickness might have originated from the conditions of measurement.

Evaluation of hardness under low temperature ageing

The low temperature ageing of polymeric materials influences the mechanical properties. The data on change of hardness of polyurethanes subjected to thermal ageing are presented in Table 5.

Table 5 Change in hardness of polyurethanes in low temperature ageing conditions

Polyurethane	Initial shore -A hardness	Final shore- A hardness	Change in shore- A hardness
HPU	88	89.4	+1.4
HPU-1	67	68.0	+1.0
HPU-2	54	55.1	+1.1
IPU	85	86.2	+1.2
IPU-1	81	81.9	+0.9
IPU-2	53	53.9	+0.9

Polymers exposed to low temperature conditions undergo virtual cross linking through hydrogen bonding. The physical cross linking once formed does not undergo dissociation under low temperature conditions. These physical cross linking combined with chemical cross linking increase the mechanical properties of cross linked amorphous polymers. All the polyurethanes exhibit a mild hardening with a small increase of 'Shore-A' hardness.

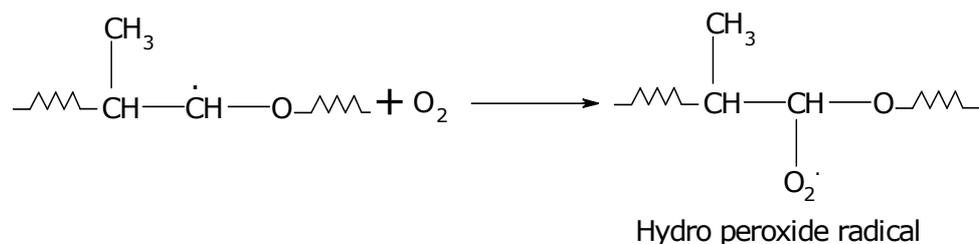
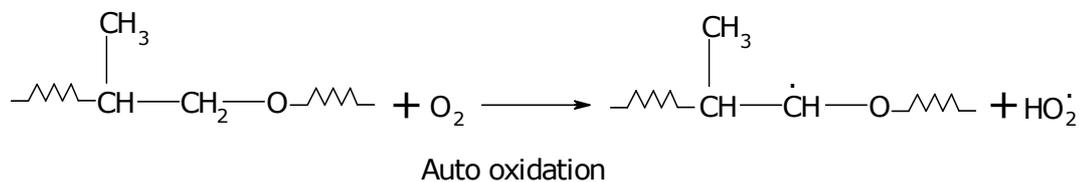
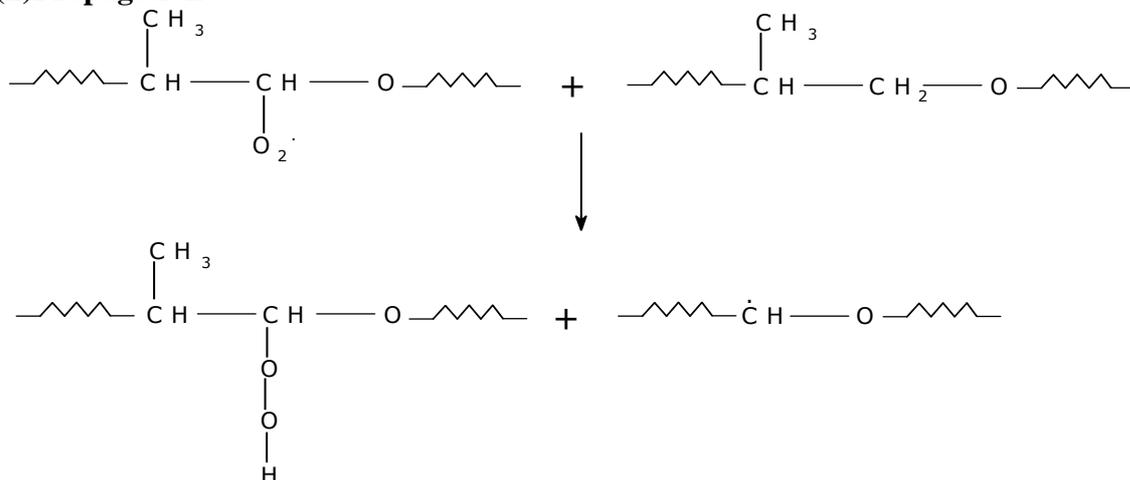
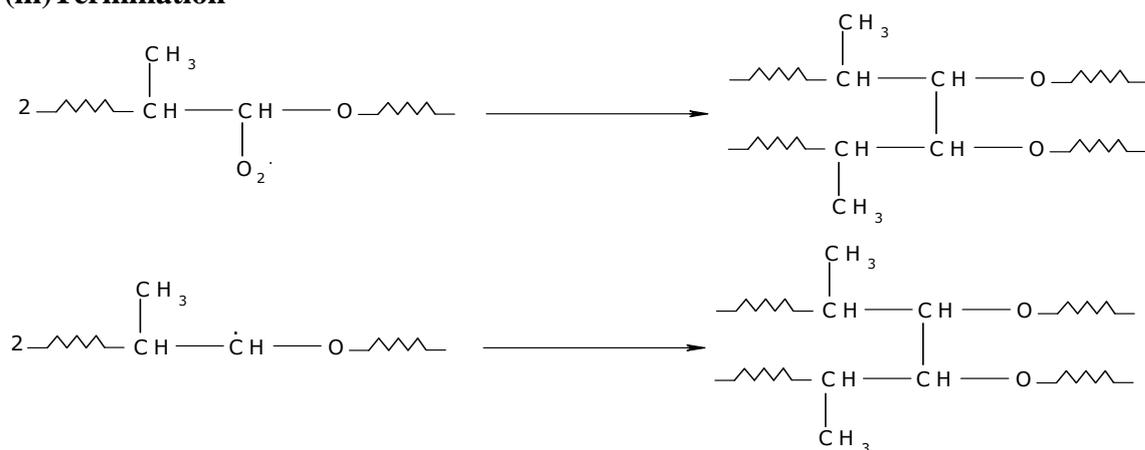
Evaluation of thermal stability at high temperature

Thermal ageing of polyurethanes leads to change of hardness and weight. Such changes are attributed to the weakening of hydrogen bonding forces and thermal oxidative degradation. The oxidative degradation in thermal ageing is mediated by the formation of radical by auto oxidation [34-35] and absorption of oxygen to produce hydroperoxide radicals. The hydroperoxide radicals abstract hydrogen present in the labile group and create macro radical. In the case of present polyurethanes the hydrogen on the carbon alpha to the ether oxygen is labile hydrogen. Hydrogen present in meta-substituted long alkyl side chain of cardanol unit, especially hydrogen present in carbon alpha to unsaturated carbons, is also a labile hydrogen as reported elsewhere for unsaturated polymers [36-37]. Therefore, production of polyurethane macro radicals and recombination of macroradicals are the possible changes in the thermal ageing. These possibilities are indicated in Scheme 3a and Scheme 3b. The weight loss and change of hardness of rigid and tough polyurethanes under thermal aging is presented in Tables 6. The weight loss was observed only with tough polyurethanes. There is no weight loss in both the case of HDI and IPDI treated hard segment polyurethanes. Interestingly, increase of hardness was observed with rigid polyurethanes HPU and IPU. This may be possibly due to cross linking of meta-substituted long alkyl side chain of cardanol.

Table 6 Change in properties of polyurethanes in thermal ageing conditions

Polyurethane	Weight loss (%)	Change in Shore- A hardness
HPU	0.00	+1.07
HPU-1	0.31	-0.69
HPU-2	0.37	-0.75
IPU	0.00	+1.02
IPU-1	0.25	-0.81
IPU-2	0.30	-0.85

Decrease of hardness was observed with polypropylene glycol-based tough polyurethanes such as HPU-1, HPU-2, IPU-1 and IPU-2. This may be due to increase of crosslinking in flexible polyol segment leading to rubber-like characteristics.

(i) Initiation**(ii) Propagation****(iii) Termination**

Scheme 3a. Oxidative degradation of polyether polyol segment of polyurethane in thermal ageing

The reason for the minimum weight loss (<1%) observed in all the HDI and IPDI treated rigid polyurethanes may be due to mild thermally induced degradation of the polymers. The Shore- A hardness was found to increase invariably in all these polyurethanes. Comparatively, significant changes observed in HDI treated tough polyurethanes are attributed to the higher possibility of surface degradation and hardening in these polyurethanes.

Table 7 Change in properties of polyurethanes in thermo-vacuum ageing conditions

Polyurethane	Weight loss (%)	Change in shore-A hardness
HPU	0.20	+1.5
HPU-1	0.31	+1.5
HPU-2	0.32	+1.7
IPU	0.19	+1.1
IPU-1	0.41	+1.2
IPU-2	0.42	+1.4

Evaluation of environmental resistance of polyurethanes

Polyurethanes can be used under many environmental conditions, but not all conditions can be tolerated. The polyether-based polyurethanes are significantly superior in humid conditions and in acidic or basic environment. They also exhibit lower hysteresis and do not heat up as easily as the polyester type [39]. In addition to their good balance of physical properties, they are inherently resistant to microbial attack and hydrolysis [40].

Table 8 Change in weight loss and mechanical properties of polyurethanes under soil burial test

Polyurethanes	Weight (g)		Tensile strength (MPa)		Elongation (%)	
	Initial	Final	Initial	Final	Initial	Final
HPU	2.225	2.225	B	B	B	B
HPU-1	2.750	2.750	16.2	16.2	126	126
HPU-2	2.520	2.520	14.6	14.6	136	136
IPU	2.671	2.671	B	B	B	B
IPU-1	2.622	2.622	28.1	28.1	141	141
IPU-2	2.550	2.550	26.0	26.0	152	152

B-Brittle

To find out the environmental resistance of the polyurethanes synthesized in the present study, soil burial test was carried out. The percentage weight loss and change in mechanical properties of the polyurethanes are presented in Table 8. There is no weight loss observed in the case of both HDI and IPDI treated polyurethanes in the soil burial test even after a period of six months. Similarly, there is also no change in the mechanical properties such as tensile strength and percentage elongation. No dimensional change and embrittlement is observed. Hence these polyurethanes are non-biodegradable.

CONCLUSION

The ageing performance shows that the HDI and IPDI treated rigid polyurethanes are stable when compared to the respective soft segment polyurethanes. The IPDI treated polyurethanes possess very good hydrolytic stability than the HDI treated polyurethanes. HDI and IPDI treated rigid polyurethanes are found to be stable towards acid, base and oxidants. But a mild weight loss is observed in the corresponding tough polyurethanes. All the polyurethanes are stable in diethyl ether. All the polyurethanes swell in dimethyl acetamide. Rigid polyurethanes are thermally stable. But the corresponding tough polyurethanes are found to undergo mild degradation. For a given isocyanate index of 1.4, the PPG-1200 added polyurethanes are found to be more stable than the PPG-2000 added analogues, due to the difference in their crosslink density. Among all, IPDI treated polyurethanes are found to be dimensionally more stable than the corresponding HDI treated polyurethanes. Since there is no weight loss, dimensional change and embrittlement observed from the environment resistance test, it is concluded that these polyurethanes are non-biodegradable.

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