

A Study on Thermal and Hydrolytic Stability of Cardanol based Polyurethanes

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ABSTRACT

Cashew nut shell liquid (CNSL) is one of the natural products obtained from cashew tree nuts (*Anacardium occidentale* Linn). Cardanol, a major constituent of CNSL is a natural alkyl phenol. It was reacted with furfuraldehyde in the presence of hydrochloric acid catalyst to give novolac resin. This resin was condensed with polyalkylene glycols and novel polyurethanes were synthesized using these polyalkylene glycol terminated cardanol furfuraldehyde novolac polyol resins, polymeric TDI and glycerol chain extender. Thermal and hydrolytic degradation of these polyurethanes were studied.

Keywords: Cardanol, furfuraldehyde, TDI, glycerol and polyurethanes.

I. INTRODUCTION

Polyurethanes are one of the most useful industrial and engineering materials with wide range of properties. Polyurethanes are composed of short, alternating poly disperse blocks of soft and hard segments. Polyurethanes exhibit broad range of mechanical and physical properties, which are tailor made for various engineering and specialty applications by varying the nature, molecular weight and composition of components in the soft and hard segments. A great number of factors such as extent of cross-linking, nature of polyols as well as R-values and conditions of curing are known to affect the properties of polyurethanes¹⁻⁴. Their properties range from liquid, soft and rubbery solids to rigid thermoplastics and thermoset materials⁵⁻¹². The polyols that are used in the synthesis of polyurethanes are based on petroleum resources, which are costly and scarce. There have been constant searches for new cost-effective renewable natural resources that can be used in the synthesis of polymers.

The increasing interest on the utilization of naturally available renewable resources for the development of

value added polymeric products has prompted to explore the potential chemical utility of naturally available cashew nut shell liquid (CNSL) raw material. Thermally treated CNSL contains more than 86% cardanol. The unique structural feature that makes cardanol an interesting monomer is the presence of a long alkyl group in the meta position.

It was planned to explore the potential chemical utility of cardanol for the preparation of novel polyurethanes. It was planned to synthesize cardanol novolac smart resins having the combined character of hard and soft segments and also can function as an active hydrogen nucleophilic compound were synthesized.

The hydroxy alkylated cardanol novolac resins were used to prepare polyurethanes using aromatic diisocyanate polymeric TDI and glycerol chain extender.

The performance of polymeric material for intended application for intended duration largely determines the service life of the product. Therefore it is essential

to evaluate the performance of polymeric material under ageing conditions. Ageing under outdoor exposure and end-use continuous exposure leads to loss of properties due to degradation of polymer. Polyurethanes are being used for variety of applications involving long-term exposure either in outdoors or in end-use environment. Such applications include storage tanks, conveyor belting, gear wheels for motor drives, castor wheels, seals and impellers in water pump, glide shoes for lift cars and cattle tags etc. Therefore it is essential to evaluate the performance of polymeric material under ageing conditions. The studies on the stability of polyurethanes under various ageing conditions were carried out.

II. Experimental

2.1 Synthesis of polyurethanes

Cardanol was separated from CNSL by vacuum distillation at 3-5mm Hg. The fraction distilled at 230-240°C was collected. Cardanol furfuraldehyde resin (C) was synthesized using cardanol and furfuraldehyde. 6 moles of cardanol was weighed into a three necked flask fitted with a Leibig condenser, ground joint thermometer and a dropping funnel. 1.0 mole of formalin was added to cardanol through the dropping funnel. 1% of hydrochloric acid was added as catalyst. The mixture was heated in a nitrogen atmosphere using a rotamandle at $150 \pm 5^\circ\text{C}$ for three hours.

1.0 mole of cardanol furfuraldehyde novolac resin and 3 moles of PEG₄₀₀ /PEG₆₀₀ were mixed in a three necked flask fitted with a Leibig condenser, ground joint thermometer and a dropping funnel. The mixture was heated in nitrogen atmosphere at $150 \pm 5^\circ\text{C}$ for three hours. The water vapor formed was removed applying vacuum at 20 mm Hg. The hydroxy alkylated cardanol novolac resins (CE1, CE2) formed was dried in vacuum and analyzed.

The polyurethanes (CE1U, CE2U) were synthesized using polyol terminated novolac resin and glycerol chain extender. Polyol terminated novolac resin and chain extender were weighed with ratio of polyol terminated novolac resin to chain extender, 87.5:12.5 and mixed.

The polyol mixture and TDI were mixed in the equivalent weight ratio to get 150 isocyanate indexes. Polyurethanes were prepared using DBTDL catalyst (0.25 % by weight) and toluene solvent.

2.2 Stability of polyurethanes

The determination of stability was mainly carried out by weight loss estimation. Neat polyurethane sheets were used for sample preparation. For all the exposures sample dimensions of 10 x 10 x 1 mm was used. Six specimens were used for each test and average value was determined. The standard deviation for the average value was maximum of 5%. An electronic balance having an accuracy of 0.001 g was used.

Thermal stability

The dimensional stability of polyurethanes was determined by exposing the sample to a temperature of 100°C for duration of 100 hrs. The samples were kept in an air oven. After 100 hrs of heating, the samples were removed, cooled to room temperature, and dimensions were measured at 28°C.

Hydrolytic stability

The ageing of polyurethanes in the media, water, alcohol, and salt solution (1N sodium chloride) was carried out for a total duration of 60 days under ambient conditions. Stability of polyurethanes in boiling water was also determined. The dimensional stability of polyurethanes was determined by immersing the samples in boiling water for duration

of 100 hrs. The samples were kept immersed in boiling water. After 100 hrs the samples were removed, cooled to room temperature, and dimensions were measured at 28°C.

Stability in organic solvents

The solubility of polyurethanes was determined in organic solvents, dimethyl acetamide (complete solvent for polyurethanes), diethyl ether, and toluene (complete solvent for phenol formaldehyde resins). Samples of uniform dimensions were cut, weighed and immersed in different solvents in an air-tight-container at 28°C for 60 days. After swelling, the specimens were wiped off and dried in vacuum till the solvent was removed completely and the constant weight after drying was noted.

Chemical resistance

The weight loss of polyurethanes was determined in hostile acidic, basic, and oxidation medium. Dilute hydrochloric (1N), sodium hydroxide (1N) and hydrogen peroxide (30%) were used.

Degradation of polyurethanes in alcoholic KOH

The degradation of polyurethanes in alcoholic KOH was determined by immersing the samples in 4 % alcoholic KOH solution. The time taken for complete dissolution of the samples was determined.

III. Results and discussion

The performance of polyurethanes under ageing conditions largely depends upon their macromolecular architecture.

Evaluation of Thermal stability

Thermal stability and dimensional stability during hot environmental conditions are important for any end

product for satisfactory functioning for intended duration of use. The data of weight loss and dimensional changes of the present polyurethanes are given in Table 1.

Table-1. Dimensional changes and weight loss of polyurethanes in thermal ageing

Polyurethane s	Change in dimension (-) (%)			Weight loss (%)
	Length h	Width h	Thickness s	
CE1U	0	0	0	0
CE2U	0	0	0	0

Dimensional changes during hot environmental conditions can occur in any polymer either due to incomplete curing of the polymer product, improper polymer processing or due to surface degradation induced by heat, ultraviolet light and outdoor weathering. Dimensional changes of cured polyurethanes under thermal ageing conditions are mediated through weakening of hydrogen bonding forces and thermal oxidation of polyether polyol soft segments.

Evaluation of hydrolytic stability

In polyurethanes, the urethane or carbamate linkage is 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 groups¹³. Allophanate group in polyurethanes also undergoes hydrolytic degradation¹⁴. The weight loss of the present polyurethane samples aged in water, methanol and sodium chloride solution (1N) are given in Table 2.

The present polyurethanes are based on multifunctional and multi segmented cardanol based polyether polyols. Hydrolytic degradation in the

present polymers is probably centered on urethane linkages associated only with the polyether polyol soft segment and also on allophanate linkages. The hydrolytic degradation in urethane linkages generates amine terminated polyurethane fragments. The hydrolytic degradation in allophanate linkages generates polyurethane fragments containing urea linkages.

Polyurethanes prepared with polyethylene glycol based cardanol resins undergo mild hydrolytic degradation in water, boiling water and methanol. This is attributed to higher water absorption character of PEG as reported by Takahara et al ^{15,16}. The water absorption on the surface of polyurethane enables surface swelling and exposure of urethane and allophanate linkages present in the hard segment for hydrolytic attack.

Ageing in sodium chloride solution (1N) does not influence the hydrolytic stability. There is no weight loss in any of the new polyurethanes in sodium chloride solution.

Table-2. Weight loss of polyurethanes in hydrolytic conditions

Polyurethane	Weight loss (%)		
	Water	Methanol	Sodium chloride solution (1N)
CE1U	0.25	0.10	0
CE2U	0	0	0

Dimensional changes and weight loss of polyurethanes in boiling water is given in Table 3. Polyurethanes based on PEG based cardanol resins undergo dimensional changes especially with the increase of thickness, which is due to the transformation to hydrophilic nature in boiling water.

Table-3. Dimensional changes and weight loss of polyurethanes in boiling water

Polyurethane	Dimensional changes (%)			Weight loss (%)
	Length	Width	Thickness	
CE1U	0	0	0.10	1.5
CE2U	0	0	0	0

The stiffening in ageing ultimately increases the hydrolytic stability of polyurethanes prepared with polypropylene glycol based cardanol resins and chain extender.

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, toluene which is compatible for dissolution of phenol formaldehyde resins and aliphatic organic solvent, dimethyl acetamide which is compatible for the dissolution of polyurethanes are selected for the present studies on the effect of organic solvents. In addition to these two organic solvents, the commonly used organic solvent *viz* diethyl ether is also used in the present study. The solvents dimethyl acetamide is found to affect the polyurethanes based on polyethylene glycol/polypropylene glycol terminated novolac polyols without/with chain extender (Table 4). However, diethyl ether is found to be inert causing no weight loss. Dimethyl acetamide was found to mildly swell the polyurethanes.

Polyurethanes based on polyethylene glycol (400)/polyethylene glycols (600) terminated novolac polyols without/with chain extender are relatively more stable in all solvents except dimethyl acetamide and toluene.

Table-4. Dimensional changes and weight loss of polyurethanes based on PEG terminated novolac polyols without/with chain extender by ageing in organic solvents

Polyurethanes	Dimethyl acetamide	Diethyl ether	Acetone	Toluene	Benzene	Carbon tetrachloride
C1E1U	0.40	0.05	0.10	0.05	0.10	0
C2E1U	0.30	0.05	0.05	0.05	0.05	0.05
C3E1U	0.25	0	0.05	0.05	0	0.05
CR1E2U	0.40	0	0	0	0.05	0
CR2E2U	0.30	0	0	0	0	0.05
CR3E2U	0.25	0	0	0	0	0
CR1E1GU	0.25	0.05	0.10	0.05	0	0
CR2E1GU	0.20	0.05	0.05	0.05	0	0
CR3E1GU	0.10	0	0.05	0.05	0	0
CR1E2GU	0.20	0	0	0	0	0
CR2E2GU	0.10	0	0	0	0	0
CR3E2GU	0.10	0	0	0	0	0

Evaluation of stability in hostile chemical environment

The hostile reactive chemical environment acid, base and oxidizing agent also induces degradation of polyurethane. Dilute acids and bases induce hydrolytic attack on polyurethane. Oxidizing agent induces oxidation of polyurethane. Acid and base-induced hydrolysis is similar to water-induced hydrolysis though the magnitude of hydrolytic degradation is larger in the case of former.

It is found that all polyurethanes except polyurethanes based on polyethylene glycol terminated novolac polyols / polyethylene glycol terminated-side chain novolac polyols with glycerol undergo hydrolytic degradation with acids and base

exposure. This is attributed to increased hydrolytic potential of hydronium ions in the case of acid. In the case of base, the abstraction of hydrogen by hydroxyl group of the base leads to hydrolysis of polyurethane.

The oxidation of polyurethane largely occurs with ether group of polyurethane^{229,230}.

The present PEG polyol -based polyurethanes undergo oxidation leading to weight loss (Tables 5 and 6). The concentration of ether groups on the surface of polyurethanes based on PEG polyol is relatively higher than in PPG polyol-based polyurethanes. Therefore degradation is more pronounced in PEG based polyurethanes.

However another possible route of oxidation could be cleavage of C-O bond forming methylene terminated radical followed by cross linking.

Table-5. Weight loss of polyurethanes based on PEG terminated novolac polyols without/with chain extender by ageing in hostile chemical environment

Polyurethanes	Weight loss (%)		
	Acid (1N)	Base (1N)	Oxidant (30% H_2O_2)
CR1E1U	0.15	0.20	0
CR2E1U	0.10	0.20	0
CR3E1U	0.10	0.05	0
CR1E2U	0.10	0.15	0
CR2E2U	0.10	0	0
CR3E2U	0	0	0.05
CR1E1GU	0.10	0.12	0
CR2E1GU	0.05	0.10	0
CR3E1GU	0.05	0.05	0
CR1E2GU	0	0	0
CR2E2GU	0	0	0
CR3E2GU	0	0	0

It is found that polyurethanes based on polyethylene glycol terminated novolac polyols / polyethylene glycol terminated-side chain novolac polyols with glycerol are more stable in hostile chemical environment.

The studies on degradation of polyurethanes in alcoholic KOH reveal that all these polyurethanes undergo dissolution in this aggressive chemical environment. However polyurethanes based on polypropylene glycol terminated novolac polyols / polyethylene glycol terminated-side chain novolac polyols with glycerol are more stable in hostile chemical environment.

Table-6. Degradation of polyurethanes based on PEG terminated novolac polyols without/with chain extender by ageing in hostile alcoholic KOH environment

Resin	Time for dissolution (Days)
CR1E1U	5
CR2E1U	5
CR3E1U	10
CR1E2U	10
CR2E2U	11
CR3E2U	15

CR1E1GU	2
CR2E1GU	5
CR3E1GU	9
CR1E2GU	32
CR2E2GU	30
CR3E2GU	35

IV. Conclusion

Chain extenders are known to improve the physical properties of polyurethanes by creating hard domains in the elastomers. For the present investigation glycerol was used as chain extender. Polyurethanes based on polyethylene glycol terminated cardanol novolac polyols with glycerol have very good stability under various ageing conditions [aqueous environment (water, methanol, boiling water), outdoor weathering (thermal ageing) and exposure to ionic salt solution].

V. REFERENCES

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