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# Ageing Characteristics of Novel Polyurethanes and Its Composites Based on Cardanol

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## ABSTRACT

Synthesis of novel polyurethanes and its composites from cardanol-based polyols were reported. Polyurethanes were synthesized from cardanol-based polyols with 4,4'-methylenebis(cyclohexyl) isocyanate and polyethylene glycol-4000. Polyurethane composites were synthesized using coir fiber with the above system. The ageing characteristics of the newly prepared polyurethanes and its composites has been studied. These studies revealed better hydrolytic, chemical and environmental resistance of rigid polyurethane and its composites when compared to tough polyurethane and its composites.

**Keywords:** Cardanol, 4,4'-methylenebis(cyclohexyl) isocyanate, polyethylene glycol-4000, coir fiber, ageing.

## I. INTRODUCTION

Polyurethanes are a prominent class of polymeric materials. Wide variety of structural changes can be produced with the different hydroxyl compounds and isocyanates leading to a wide spectrum of properties and applications[1]. It contains a high concentration of polar groups, in particular the urethane group, resulting from isocyanate-hydroxyl reactions. The interactions between these polar entities are of great importance in determining the properties of polyurethane of all types[2] besides the composition and characteristic of the polyol, diisocyanates and the additives utilized during the synthesis[3].

Polyurethane composites have good wear resistance and excellent mechanical properties and it is easy to adjust their hardness by changing the ratio of hard and soft segments. As a result, they are an important class of materials for structural and tribological applications that is, to do with interactions of moving surfaces such as friction or lubrication. They are used in a wide range of applications areas such as bearings, gears, aerospace, automobiles, construction, biomedical, commercial and domestic sectors including sports industry, household appliances, packaging, etc.[4-6].

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[7,8].

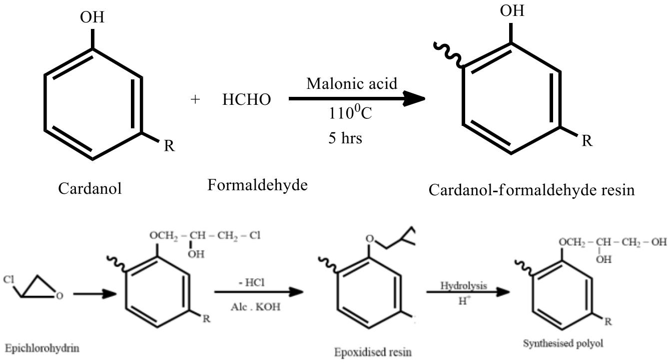
## II. METHODS AND MATERIAL

### 2.1 Materials

Cardanol was obtained from M/s Satya Cashew Chemicals Pvt. Ltd., Chennai. Formaldehyde (40% solution), and malonic acid and methanol were received from Merck, Mumbai. Epichlorohydrin was obtained from Sisco Research Laboratoies Pvt. Ltd., Mumbai. 4,4'-methylenebis(cyclohexyl) isocyanate and dibutlytin dilaurate was received from Aldrich Chemicals, Bangalore. Polyethylene glycol-4000(PEG-4000) was received from Sisco Research Laboratoies Pvt. Ltd., Mumbai. The chemicals were used as received. Coir fiber was procured from local sources.

### 2.2 Synthesis of cardanol-based polyols

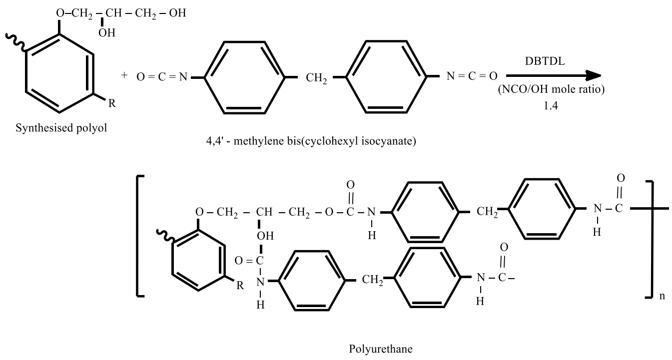
Cardanol-based polyols were synthesized by the condensation of cardanol and formaldehyde using malonic acid as catalyst. Cardanol was taken in a three necked flask equipped with a Liebig condenser, mechanical stirrer and thermometer. Formaldehyde and 1% malonic acid catalyst in methanol was added to the cardanol through a dropping funnel. The reaction was carried out at temperature $110^o \pm 5^oC$ for 5 h. After, it was reacted with epichlorohydrin at $60^oC$ for 4 h to obtain epoxidized resins. Finally, cardanol-based polyols were synthesized from epoxidized resins using methanol, the epoxide ring was opened at $60^oC$ for 30 min (Scheme 1).



**Scheme 1.**Formation of cardanol-based polyol

## 2.3 Synthesis of polyurethanes and its composites

Rigid polyurethane (CDPU) was prepared by the reaction of cardanol-based polyol (synthesized polyol) with 4,4'- methylenebis(cyclohexyl) isocyanate keeping the isocyanate index 1.4. The reaction was carried out at room temperature using the catalyst dibutyltin dilaurate. The polymer was allowed to cure for 24 h in a flat surface and again cured in a vacuum oven at 80°C for 48 h (Scheme 2). Similarly, tough polyurethane (CDTPU) was prepared from commercial polyol, polyethylene glycol-4000(PEG-4000) with the above system. The composites (CDPU 5%, CDPU 10% and CDTPU 5%, CDTPU 10%) have been synthesized by incorporating the coir fiber (5% and 10%) into the polyurethanes.



**Scheme 2.** Formation of polyurethane

## 2.4 Ageing characteristics of polyurethanes and its composites

The studies on the stability of polyurethanes and its composites under various ageing conditions were carried out using the general guidelines of ASTM standards. The conditioning as well as specimen preparation was followed using appropriate procedure discussed in the following sections. The determination of stability was mainly carried out by weight loss estimation. Neat polyurethane sheets were used for sample preparation.

### A. Determination of weight loss in hydrolytic conditions

The weight loss of polyurethanes and its composites in the media, water, ethanol and salt solution (1N sodium chloride) were estimated. Polyurethane samples (3 x 1 x 0.1 cm) were immersed in the medium (100 ml) for a total duration of 60 days under ambient conditions. The medium was changed and fresh medium was added at an interval of one week. An electronic weighing balance having an accuracy of 0.001 g was used.

### B. Determination of weight loss in hostile chemical environment

The degradation of polyurethanes and its composites in hostile acidic, basic and oxidation medium was studied. Dilute hydrochloric acid (1N), sodium hydroxide (1N) and hydrogen peroxide (30%) were used. The medium was changed and fresh medium was added at the interval of one week. The samples were removed at the end of exposure, dried and weighed.

### C. Determination of weight loss in organic solvents

The solubility of polyurethanes and its composites was determined in organic solvents, viz., ethyl methyl ketone, chloroform, toluene, acetone and dimethyl acetamide. Polyurethane samples were conditioned and weighed before exposing to solvent. The sample was immersed in solvent in an air-tight-container at 23°C for 60 days. The sample was removed and dried under vacuum and weighed.

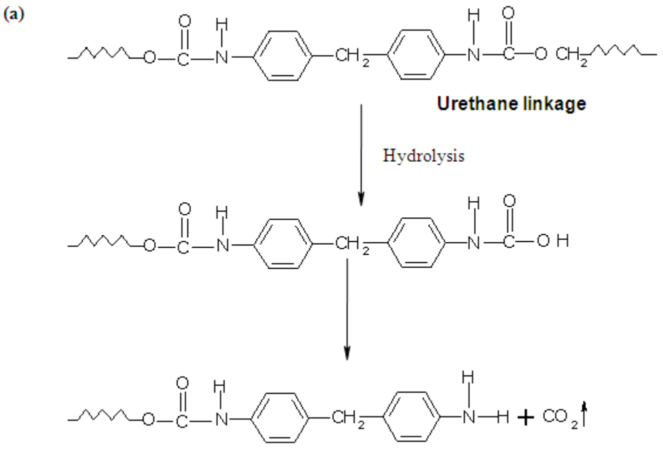
### D. Determination of stability of polyurethanes and its composites under thermal ageing

The stability of polyurethanes and its composites under prolonged exposure in thermal environment (thermal ageing) was evaluated. The conditioned samples were kept in an oven 60°C. Then the samples were removed from the oven, cooled to ambient temperature and weighed.

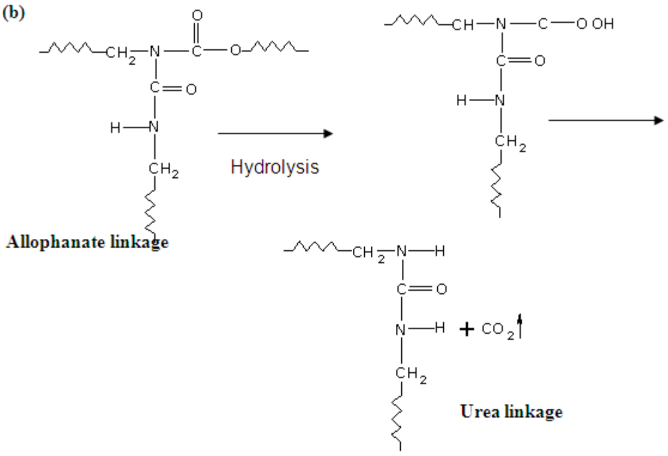
## III. RESULTS AND DISCUSSION

### A. Hydrolytic degradation in polyurethanes and its composites

There is no weight loss in any of the newly synthesized rigid polyurethane and its composites. However, a small weight loss is observed in the case of all the tough polyurethanes and the composites in water, ethanol and salt solution. 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[9]. This is attributed to the lower crosslink density. The hydrolytic attack on polyether polyol-based polyurethane is centered mainly on urethane group. Allophanate group in polyurethanes also undergo hydrolytic degradation. 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 in accord to the Scheme 3 (a) and (b). The weight loss of the polyurethanes and its composites have been presented in Table 1.



**Amine Termination**



**Scheme 3 (a) and (b)**
Hydrolytic degradation in polyurethane

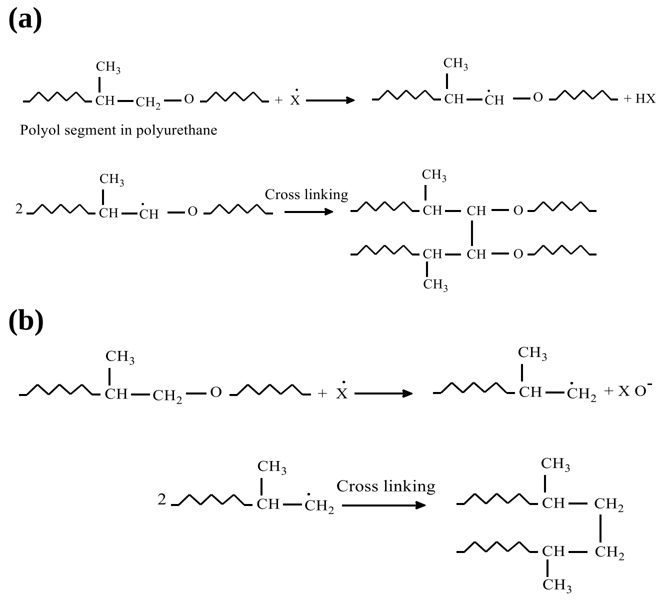
**Table 1**
Weight loss of polyurethanes and its composites under hydrolytic conditions

| Polyurethanes and the composites | Weight loss (%) | | |
|---|---|---|---|
| | Water | Ethanol | Salt solution (in NaCl) |
| CDPU | 0 | 0 | 0 |
| CDPU 5 | 0 | 0 | 0 |
| CDPU 10 | 0 | 0 | 0 |
| CDTPU | 0.05 | 0.07 | 0.06 |
| CDTPU 5 | 0.04 | 0.06 | 0.05 |
| CDTPU 10 | 0.02 | 0.04 | 0.03 |

### B. Oxidative degradation of polyurethane hostile chemical environment

It has been found that rigid polyurethane and its composites are stable towards acid, base and oxidant. But, there is a slight percentage of degradation in tough polyurethane and its composites as presented in Table 2.

The hydrolytic degradation of the tough polyurethane and its composites 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[10]. For the tough polyurethane and its composites, the concentration of ether group is found to be relatively higher than rigid polyurethane and its composites. Hence, degradation is more prominent in tough polyurethane and its composites leading to weight loss. 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 as given in Scheme 4.



X = peroxide radical

**Scheme 4.** Oxidative degradation of polyurethane in hostile chemical environment

**Table 2**

Weight loss under hostile chemical environment

| **Polyurethane and its composites** | **Weight loss (%)** | | |
|---|---|---|---|
| | **Acid (1N HCl)** | **Base (1N NaOH)** | **Oxidant (30% $H_2O_2$)** |
| CDPU | 0 | 0 | 0 |
| CDPU 5 | 0 | 0 | 0 |
| CDPU 10 | 0 | 0 | 0 |
| CDTPU | 0.07 | 0.05 | 0.04 |
| CDTPU 5 | 0.04 | 0.03 | 0.03 |
| CDTPU 10 | 0.01 | 0.02 | 0.01 |

### C. Stability of polyurethanes and the composites in organic solvents

There is no weight loss in rigid polyurethane and its composites. The solvents are found to affect the tough polyurethane and its composites and the weight loss as shown in Table 3.

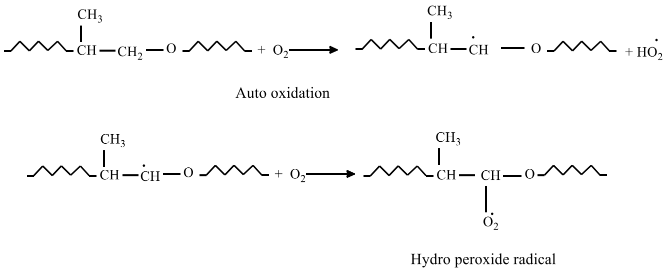
**Table 3.** Weight loss of polyurethanes and its composites under organic solvents

| **Polyurethane and its composites** | **Weight loss (%)** | | | | |
|---|---|---|---|---|---|
| | **EMK** | **Chloroform** | **Toluene** | **Acetone** | **DMA** |
| CDPU | 0 | 0 | 0 | 0 | 0 |
| CDPU 5 | 0 | 0 | 0 | 0 | 0 |
| CDPU 10 | 0 | 0 | 0 | 0 | 0 |
| CDTPU | 0.09 | 0.07 | 0.05 | 0.12 | 0.29 |
| CDTPU 5 | 0.08 | 0.07 | 0.05 | 0.12 | 0.26 |
| CDTPU 10 | 0.07 | 0.06 | 0.04 | 0.09 | 0.24 |

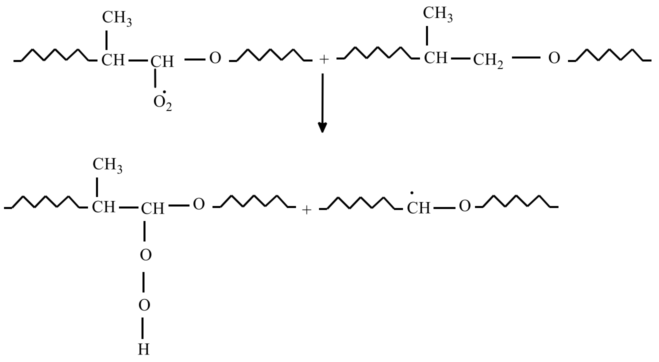
### D. Stability of polyurethanes and the composites under thermal ageing

Thermal ageing of polyurethanes and its composites leads to change in 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 and absorption of oxygen to produce hydroperoxide radicals. The hydroperoxide radicals abstract hydrogen present in the labile group and create macro radical. Hydrogen present in meta-substituted long alkyl side chain of cardanol unit, especially hydrogen present in carbon alpha to unsaturated carbons, is labile hydrogen as reported. Therefore, production of polyurethane macro radicals and recombination of macro radicals are the possible changes in the thermal ageing[11]. These possibilities are indicated in Scheme 5 (a) and Scheme 5 (b). There is no weight loss for rigid polyurethane and its composites, however, weight loss occurs for tough polyurethane and its composites under thermal ageing has been presented in Table 4. This may be due to crosslinking of meta-substituted long alkyl side chain of cardanol.

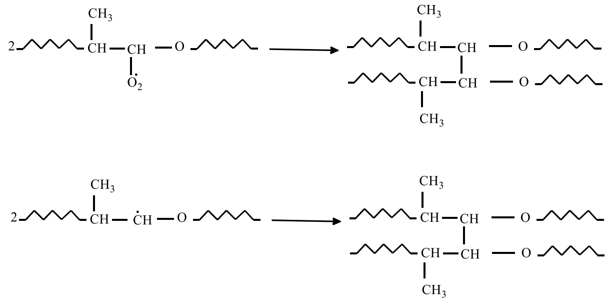
**(i) Initiation**



**(ii) Propagation**



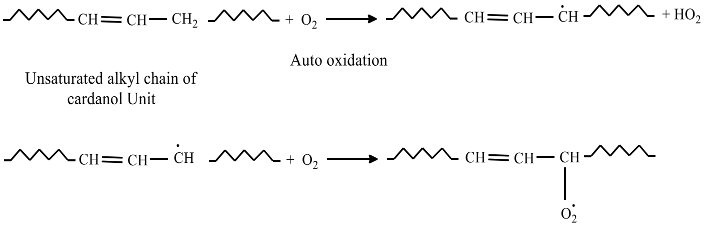
**(iii) Termination**



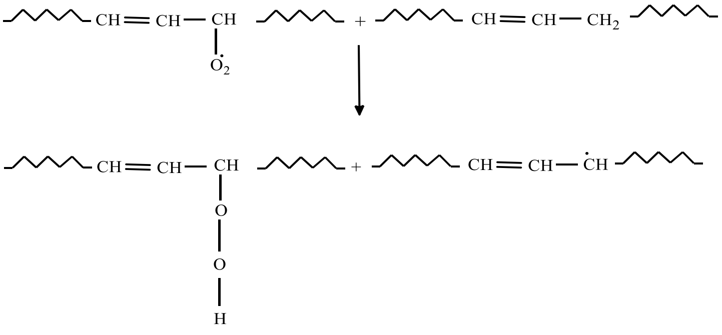
**Scheme 5 (a)**

### Oxidative degradation of polyether polyol segment of polyurethane in thermal ageing

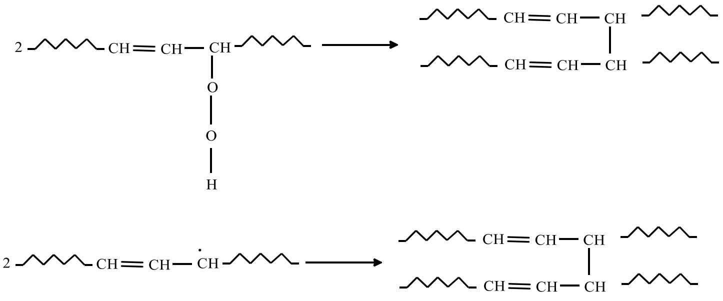
**(i) Initiation**



**(ii) Propagation**



**(iii) Termination**



**Scheme 5 (b).** Oxidative degradation of cardanol unit in thermal ageing

**Table 4.** Weight loss of polyurethanes and its omposites under thermal ageing

| Polyurethane and its composites | Weight loss (%) |
|---|---|
| CDPU | 0 |
| CDPU 5 | 0 |
| CDPU 10 | 0 |
| CDTPU | 0.06 |
| CDTPU 5 | 0.04 |
| CDTPU 10 | 0.03 |

## IV. CONCLUSION

The ageing characteristics shows that rigid polyurethane and its composites are stable when compared to tough polyurethane and its composites. Also, it possess very good hydrolytic stability than the tough polyurethane and its composites. Rigid polyurethane and its composites are thermally stable. But the tough polyurethane and its composites are found to undergo mild degradation due to lower crosslink density.

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