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Ageing studies of cardanol based polyurethanes

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ABSTRACT

Hard segment polyurethanes based on cardanol-furfural resins have been synthesized using diphenylmethane diisocyanate and toluene diisocyanate. Soft segment polyurethanes have been produced by condensing the commercially available polyol, polypropylene glycol-1200 (PPG-1200) with the above system. The chemical ageing such as hydrolytic stability (water, alcohol and salt solution), chemical stability (acid, base and oxidizing agents exposure), stability in organic solvents and the physical ageing like dimensional stability under high and low temperature, thermal stability and thermo-vacuum stability have been undertaken and the results are discussed. The evaluation of ageing performance reveals that the MDI- and TDI- treated hard segment polyurethanes are more stable than the corresponding soft segment polyurethanes. The biodegradability of polyurethanes have been tested by the soil burial test and assessed by SEM analysis.

Key words: Cardanol, polyurethane, stability, biodegradability, SEM analysis

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INTRODUCTION

Since the first developments of polymeric materials, scientists and engineers have made intensive efforts to increase the stability of these materials with regard to their diverse environmental influences. As a result, polymeric materials are now used in all sectors of life as very durable products with tailor-made properties. Among the polymeric materials, polyurethanes appear in an astonishing variety of forms, making them the most versatile of any family of plastic materials. Comfortable durable mattresses and automotive and domestic seating are manufactured from flexible foam. Rigid polyurethane foam is one of the most effective practical thermal insulation materials, used in applications ranging from domestic refrigerators to large industrial buildings. Polyurethane adhesives are used to make a wide variety of composite wood products from load-bearing roof beams to decorative cladding panels. Manufacturers of polyurethane materials are increasingly being asked for assurance of product lifetime, particularly for components, which cannot be easily inspected or may fail catastrophically in service. Polyurethanes are increasingly being used in a wide range of applications where long-term service in hostile environments is required. The stability of a polymer deals with their degradation reactions and their control which are a major preoccupation of practitioners of many and diverse aspects of modern polymer technology.

Numerous papers have been published on the degradation of polyurethanes, including hydrolysis, thermolysis, oxidation initiated by heat and light, microbial degradation, degradation at high temperatures during burning, etc. Due to the fact that commercial polyurethanes are chemically complex and contain thermally and hydrolytically labile groups such as urea, biuret, allophanate, isocyanurate, ether and ester moieties, as well as various additives, it is not simple to assess their present state of stability and remaining service life.

Polyurethanes have increased tensile strength and melting points making them more durable [1]. Their resistance to degradation by water, oils, and solvents make them excellent for the replacement of plastics [2]. As coatings, they exhibit excellent adhesion to many substances, abrasion resistance, electrical properties and weather resistance for industrial purposes [2,3]. Polyurethanes are frequently used in underwater applications. They are required to resist the marine environment over long periods of immersion and their stability in sea water has been studied [4]. Murata *et al.* discussed the hydrolysis resistance of polyurethanes and showed the importance of the diol chemistry on molecular weight stability in water [5]. Rutkowska *et al* examined the degradation of polyester- and polyether-based polyurethanes in sea water for periods up to 12 months and showed the significantly higher strength retention of the latter [6]. A recent review of elastomers used in the offshore industry described different modes of deterioration, including mechanical degradation, chemical changes and cracking due to UV and ozone attack [7]. The influence of ageing is often followed by measurement of tensile properties, as this is one of the easiest tests to perform. Compression set and sealing force measurements have also been employed, for joint life applications [8]. Ageing of polyurethane foam Insulation in simulated refrigerator panels have been studied by Kenneth *et al*[9]. Appreciable hydrolytic, oxidative and chemical stability could

be observed with castor oil based potting compounds of hexamethylene diisocyanate – trimethylol propane (HDI-TMP) adduct for fabrication of haemodialyzer [10]. Polyurethanes synthesized using castor oil and multifunctional isocyanate have excellent hydrolytic stability due to a higher degree of crosslinking through castor oil unit [11-13].

Polyurethanes have been extensively used and tested in different biomedical applications. Cardiac valves and ocular implants are examples of permanent implantable devices prepared by polyurethanes [14-17]. Despite of their excellent mechanical properties and good biocompatibility [18], their long-term molecular stability in a dynamic *in vivo* environment is limited [19]. Poly (ester urethanes), largely applied as biomaterials for medical devices, can be hydrolyzed chemically and enzymatically in the aliphatic ester linkage. Poly (ether urethanes) have usually higher hydrolytic stability than poly (ester urethanes), and have been used as medical scaffolds for years [20]. However, it is known actually that poly (ether urethanes) can be degraded by either oxidative processes mediated by neutrophils and monocyte-derived macrophages or hydrolytic processes catalyzed by enzymes [21].

Degradation studies on segmented polyurethanes prepared with hexamethylene diisocyanate, poly (caprolactone) and different chain extenders in acid and alkaline media have also been studied [22]. Yanhong Zhang *et al* studied the degradation of waterborne polyurethane based on toluene diisocyanate [23]. Chemical degradation of microporous polyurethane elastomer by diethyl phosphonate or tris (1-methyl-2-chloroethyl) phosphate treatment has been studied [24, 25]. It has been reported that the chemical degradation of flexible polyurethane foams based on toluene diisocyanate and polyester polyol or polyether polyol by treatment with triethyl phosphate [26]. UV-aging of thermoplastic polyurethane material has been also evaluated [27]. This paper deals with the ageing studies of the synthesized polyurethanes based on cardanol-furfural resins under different chemical and thermal environment. The biodegradability has also been tested by soil burial test.

MATERIALS AND METHODS

EXPERIMENTAL

Materials

Cardanol was obtained from M/s Sathya Cashew Pvt.Ltd., Chennai, India. Furfural (AR.grade) was received from M/s S.D.Fine chemicals, Adipic acid, diphenylmethane diisocyanate and toluene diisocyanate were received from E.Merck (Germany), Methanol (BDH) was used to dissolve the catalyst. PPG-1200 was received from Aldrich chemicals(USA) and dibutyltin dilaurate was received from Fluka Chemie (Germany).The chemicals were used as received.

Synthesis of polyurethanes

Novolac resin with mole ratio, i.e., 1:0.7 of cardanol to furfural was prepared using adipic acid as catalyst. The cardanol-furfural resin was maintained under vacuum for 2 h before polymerization. The hard segment polyurethanes(PUM and PUT) were prepared by mixing the cardanol-furfural resin with two different diisocyanates viz., 4,4'-diphenyl methane diisocyanate and toluene diisocyanate, keeping the isocyanate index (NCO/OH mole ratio) constant at 1.4. The reaction was carried out at room temperature in the presence of dibutyltin dilaurate as catalyst. Similarly the soft segment polyurethanes(PUMP and PUTP) were prepared by treating the cardanol-furfural resin and the commercially available polyol, polypropylene glycol-1200,(PPG-1200) with two different diisocyanates viz.,4,4'-diphenyl methane diisocyanate and toluene diisocyanate, keeping the isocyanate index (NCO/OH mole ratio) constant at 1.4. The polyurethanes formed were then allowed to cure for 48 h in a flat surface without any disturbance. The polyurethanes were again cured in a vacuum oven at 80°C for 48 h. The well cured polyurethanes were subjected to ageing studies.

Ageing performance of polyurethanes

The stability of polyurethanes under various ageing conditions has been studied by using the general guidelines of ASTM standards. The weight loss estimation method is used to determine the stability of the polyurethanes. The ageing characteristics of both the hard and soft segment polyurethanes of novolac resin were carried out using neat polyurethane sheets of dimensions 3 x 1 x 0.1 cm conditioned at $25^{\circ} \pm 1^{\circ}\text{C}$ and $50 \pm 5\%$ 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 at the interval of one week. The weight loss was determined.

Chemical resistance test

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 in organic solvents such as dimethyl acetamide, diethyl ether and toluene were carried out according to ASTM C 267. The conditioned samples were kept in 100 ml of the organic solvent 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.

Thermal stability (shape changes) under low temperature

The shape changes of polyurethanes under low temperature ageing were carried out according to ASTM D 756. Shore-A hardness was determined for conditioned samples. Then the samples were kept in low temperature cabinet at 40C for a period of 60 days. After 60 days, the samples were subjected to shore hardness determination. The changes of hardness were determined.

Thermal stability (weight loss) under high temperature

The thermal ability of polyurethanes 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 bio-degradability

The environmental resistance of the synthesized polyurethanes was carried out using soil burial test. 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 hydrolytic attack on polyether polyol-based polyurethane is centered mainly on urethane group. Allophanate group in polyurethanes also undergoes hydrolytic degradation [28]. The hydrolysis at urethane linkage leads to amine termination. The hydrolysis at allophanate linkage leads to the formation of urea-linkage. Hydrolytic and enzymatic degradation decreased with the increase of the diol carbon chains in polyol, and increased by substituting aromatic diisocyanate with aliphatic diisocyanate [29]. It is considered that hydrophobicity and hard segment formation seem to resist the hydrolytic and enzymatic degradation of polyurethanes. In general, the hydrolytic stability of polyurethanes can be related to that of their polyol component, with the stability of the poly ether segments being greater than the polyester. In addition it has been found that the longer the hydrocarbon chain of the glycol portion, the more resistant the polyurethane is to hydrolysis [30].

Table 1: Weight loss of polyurethanes based on cardanol-furfural resins in different chemical environment

Polyurethane	Water	Ethanol	NaCl	1N HCl	1N NaOH	30% H ₂ O ₂	Diethyl ether	Toluene	DMA
PUM	0	0	0	0	0	0	0	0	+79.4
PUT	0	0	0	0	0	0	0	0	+74.7
PUMP	0	0	0	0.49	1.70	0.20	0	1.44	+84.3
PUTP	0	0	0	0.55	1.55	0.29	0	1.80	+80.2

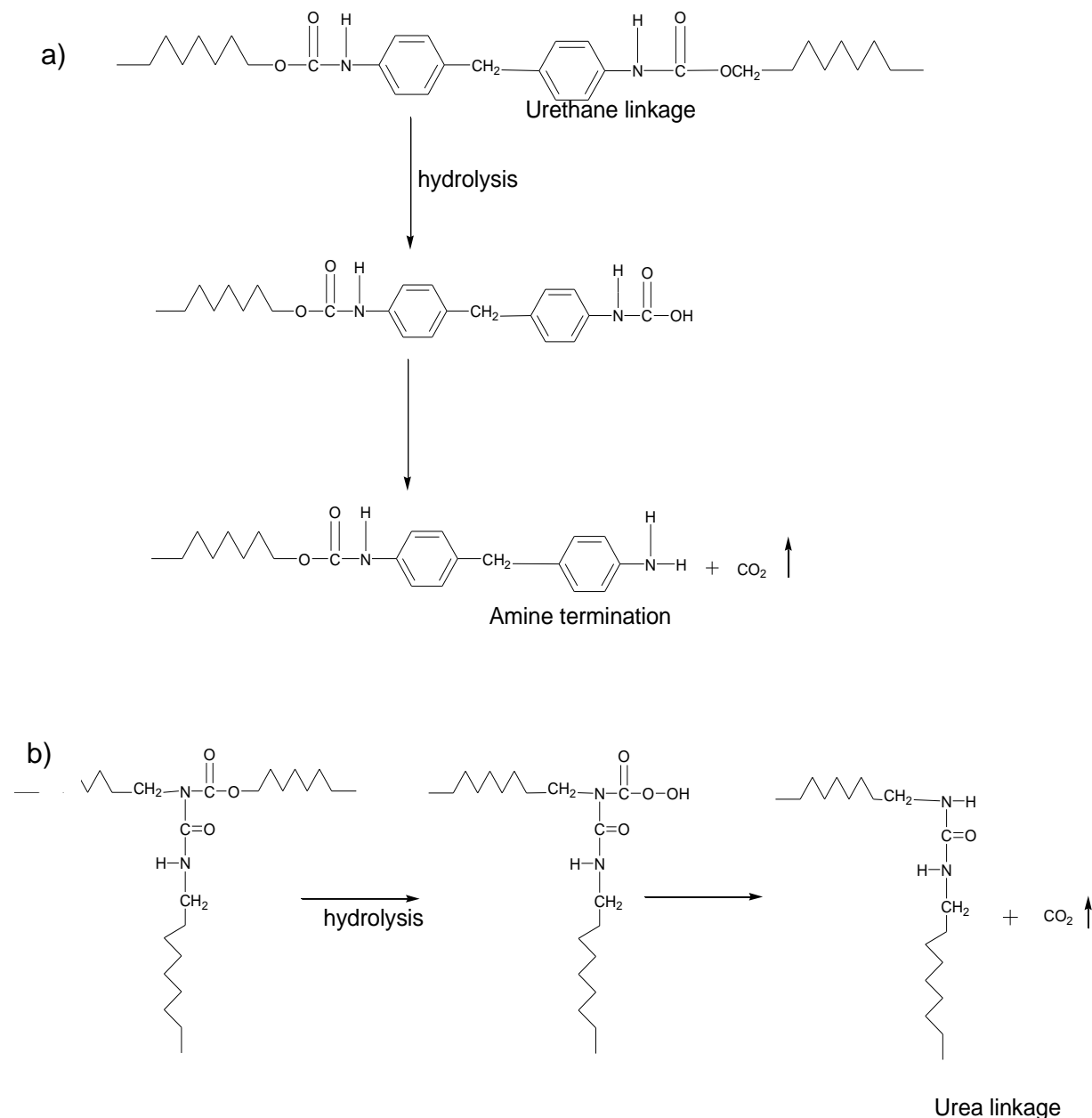
The different media under study has the same influence on the hydrolytic degradation. The polyurethanes matrix is less susceptible to ionic permeation and hence the sodium ions and chloride ions have less effect on the degradation [31]. There is no weight loss of polyurethanes based on cardanol-furfural resins under hydrolytic conditions. Hence all the synthesized polyurethanes are found to possess very good hydrolytic stability (Table 1).

The degradation of polyurethanes is also induced by the chemical environments such as acid, base and oxidizing agent. The hydrolytic degradation is induced not only by water but also by acids and bases. Oxidizing agent helps degradation of polyurethanes by the oxidation reaction.

From the results obtained (Table 1), it has been found that both diphenyl methane diisocyanate (MDI) and toluene diisocyanate (TDI) treated hard segment polyurethanes based on cardanol – furfural resins are stable towards acid, base and oxidant. But in the case of soft segment polyurethanes obtained by the addition of commercial polyol, polypropylene glycol-1200 (PPG-1200) in acidic and basic medium, there is a very small percentage of degradation (≈ 0.5 -1.75). In the case of oxidant the percentage of weight loss ranges from 0.20-0.30.

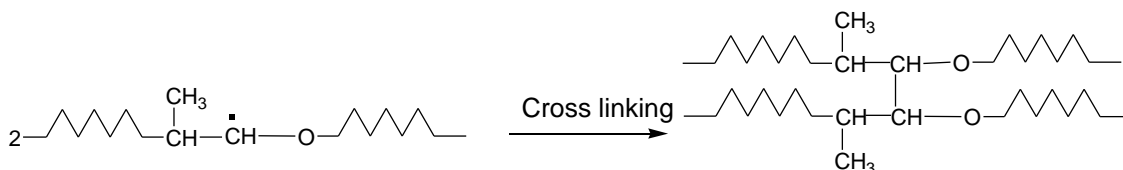
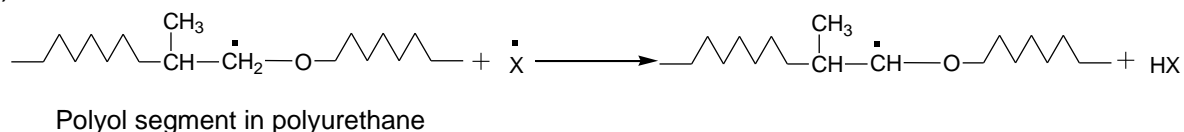
The hydrolytic degradation of the soft segment polyurethanes in acid medium may be due to increase of hydronium ions. The base induced hydrolytic degradation is due to the abstraction of hydrogen by hydroxyl group of the base. The Scheme of hydrolytic degradation is presented in Scheme 1a and Scheme 1b.

The oxidation of polyurethanes is mediated by abstraction of labile hydrogen on the carbon alpha to the ether oxygen as presented in Scheme 2a. There is another possible route of oxidation in which cleavage of C-O bond leads to methylene terminated radical followed by cross-linking as shown in Scheme 2b. The mild degradation of soft segment polyurethanes may be due to their nature of cross linked structure.

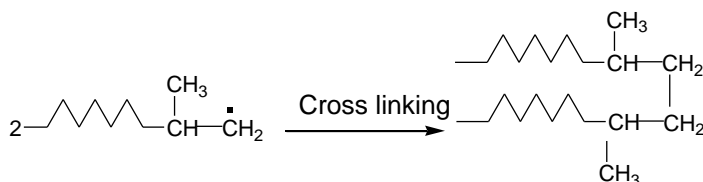
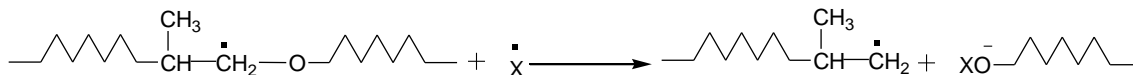


Scheme 1. Hydrolytic degradation in polyurethanes

a)



b)



Scheme 2. Oxidative degradation of polyurethane in hostile chemical environment.

The organic solvents also influence the stability of polyurethanes by solvation and dissolution of polymers. Three solvent systems are chosen namely, the aromatic organic solvent, toluene which easily dissolves the phenolic resins, the aliphatic organic solvent, dimethyl acetamide which is compatible for the dissolution of polyurethanes and the widely used organic solvent, diethylether to study the stability of the synthesized polyurethanes. All the synthesized polyurethanes are stable towards diethylether. Both MDI and TDI treated hard segment polyurethanes based on cardanol-furfural resins are stable towards toluene. But toluene has little influence on the degradation of soft segment polyurethanes based on cardanol-furfural resins and the percentage of weight loss ranges from 1.44-2.00. All the polyurethanes are found to swell in dimethyl acetamide. DMA is found to penetrate into the polyurethane matrix and causes increase in weight to about 85% (Table 1). The degree of swelling varies with degree of crosslink density.

Dimensional stability is a measurement of a material's change in dimensions such as the length, width and thickness in response to various environmental exposure conditions. There are no dimensional changes in the length wise and breadth wise in all the polyurethanes. The MDI - treated and TDI - treated hard segment polyurethanes based on cardanol-furfural resins are dimensionally stable towards thermal ageing. But a small change in the thickness (about 0.75%) of the corresponding soft segment polyurethanes is observed due to mild surface degradation and thermal oxidation.

The mechanical properties of polymeric materials are influenced by thermal ageing methods. When the polymers are exposed to low temperature, further cross linking take place through hydrogen bonding. The physical cross linking once formed does not undergo dissociation under low temperature conditions. The combination of physical and chemical cross linking leads to increase in the mechanical properties. All the synthesized polyurethanes experienced a mild hardening and hence a small increase in shore - A hardness($\approx 1.5\%$) is observed.

It is observed that all the polyurethanes exhibit the change in weight and shore-A hardness under high temperature. No weight loss is observed in the case of hard segment polyurethanes based on cardanol-furfural resins. But shore-A hardness increases to about 1.12% in the case of MDI - treated hard segment polyurethanes and 1.21% in the case of TDI - treated hard segment polyurethanes. The MDI - treated soft segment polyurethanes based on cardanol-furfural resins showed the percentage of weight loss of about 0.42% and the shore-A hardness decreases to about 1%. In the case of TDI- treated soft segment polyurethanes, the percentage of weight loss of about 0.45% is observed and the decrease of shore-A hardness is about 1.2%

The oxidation reaction does not take place under thermo vacuum conditions and hence the vacuum induced thermal effect is observed in the polyurethanes under study. Less than 1% weight loss is observed in all the synthesized polyurethanes. This may be due to mild thermal degradation of the polyurethanes and the increase in shore-A hardness ranges from 1.3 to 1.9%.

Biodegradability of polyurethanes

Very small variations in the chemical structures of polymer could lead to large changes in their biodegradability. The biodegradability depends on the molecular weight, molecular form and crystallinity. It decreases with increase in molecular weight, while monomers, dimers and repeating units degrade easily. Polyurethane produced by the diisocyanate polyaddition process is the characteristic chain link of urethane bond. Growth of microorganisms could not be supported by polyurethanes and so the biodegradation was also found incomplete. Polyurethane degradation proceeded in a selective manner, with amorphous regions. Also, polyurethanes with long repeating units and hydrolytic groups would be less likely to pack into high crystalline regions as normal polyurethane, and these polymers were accessible to

biodegradation. Although cross linking was considered to inhibit degradation, some micro organisms like papain were found to diffuse through the film and break the structural integrity by hydrolyzing the urethane and urea linkage producing free amine and hydroxyl group [32].

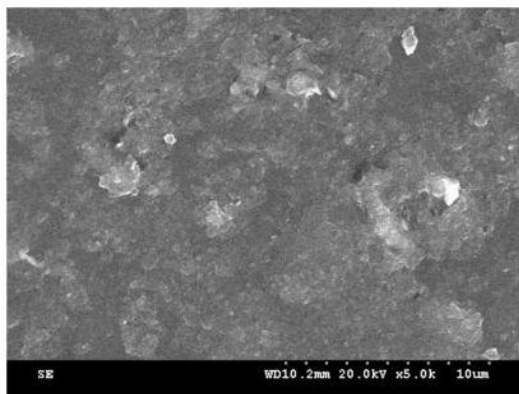


Figure 1. SEM photograph of PUM (before soil burial test)

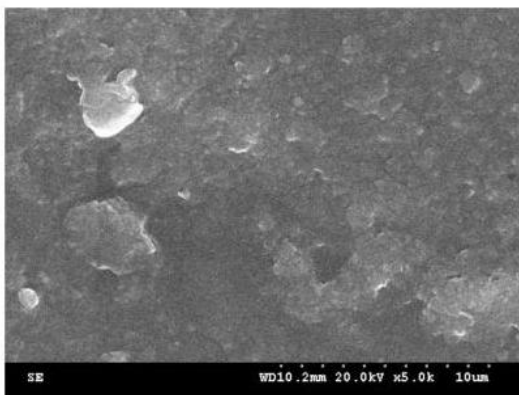


Figure 2. SEM photograph of PUM (after soil burial test)

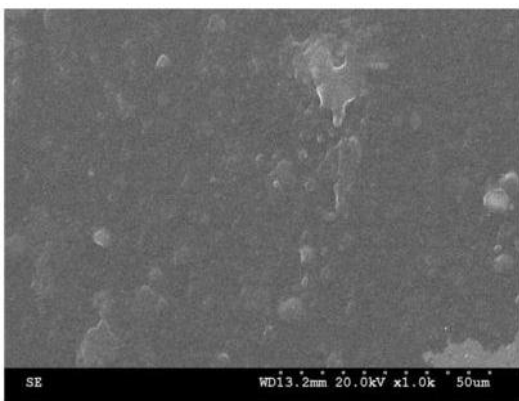


Figure 3. SEM photograph of PUMP (before soil burial test)

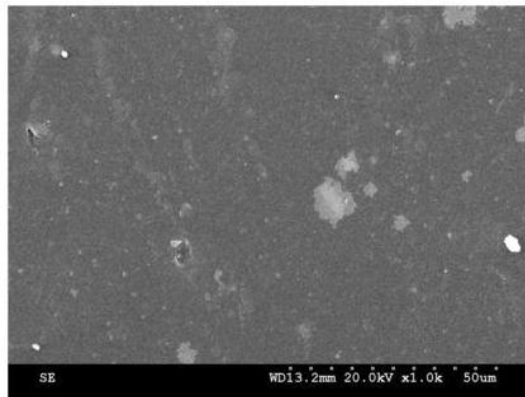


Figure 4. SEM photograph of PUMP (after soil burial test)

In the present study, the environmental resistance of the synthesized hard and soft segment polyurethanes has been studied by the soil burial test. The synthesized polyurethanes do not exert any weight loss and change in mechanical properties in the soil burial test even after a period of six months. From the observation of soil burial test, it has been concluded that the synthesized polyurethanes are not biodegradable. The SEM photographs of two representative polyurethanes before and after burial test are presented in Fig. 1, Fig. 2, Fig. 3 and Fig. 4. The SEM reports also support the fact that the synthesized polyurethanes are non-biodegradable.

CONCLUSION

The evaluation of ageing performance reveals that the MDI - treated and TDI - treated hard segment polyurethanes based on cardanol-furfural resin are more stable than the corresponding soft segment polyurethanes. All the polyurethanes exhibit very good hydrolytic stability. The MDI-treated/TDI- treated hard segment polyurethanes based on cardanol-furfural resin are thermally and dimensionally more stable and having more resistivity towards acid, base and oxidizing agent. But the corresponding soft segment polyurethanes experienced a little weight loss on exposure to these chemicals and thermal conditions. They are dimensionally less stable. All the synthesized polyurethanes undergo swelling in dimethyl acetamide. There is no weight loss, shape change or embrittlement due to environmental exposure in the bio-degradability test which indicates that these polyurethanes are non-biodegradable.

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