

ORIGINAL ARTICLE

Synthesis and Ageing studies of cardanol based polyurethanes from Castor Oil- Toluene diisocyanate

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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. Interpenetrating polymer networks were prepared from castor oil, toluene-2, 4-diisocyanate and cardanol based dye monomer with 4-chloroaniline. Such biopolymers prepared using benzoyl peroxide as initiator and ethylene glycol dimethacrylate as cross-linker. 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 biodegradability of polyurethanes have been tested by the soil burial test and assessed by SEM analysis. In addition to the effect of change in NCO/OH molar ratio of polyurethane, was also studied.

Keywords: Cardanol; cardanol based dyes; polyurethanes, biodegradability, SEM analysis

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INTRODUCTION

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 synthesis of polyurethane using castor oil and toluene diisocyanate in different NCO/OH molar ratios to give a series of polyurethanes (PUs) along with the particular composition of the synthesized cardanol based dye monomers in presence of Benzoyl Peroxide (BPO) which acts as initiator and ethylene glycol dimethacrylate (EGDM) as cross-linker to give a number of interpenetrating polymer networks (IPNs). The ageing studies of the synthesized IPNs under different chemical and thermal environment. The biodegradability has also been tested by soil burial test.

MATERIALS AND METHODS

Cardanol was obtained from M/s Satya Cashew Chemicals Ltd, Chennai, Formaldehyde (40%) solution; sodium nitrite, potassium hydroxide and methanol were received from M/s BDH Ltd (India). Toluene diisocyanate and ethylene glycol dimethacrylate were received from Aldrich chemicals (USA) and Benzoyl peroxide and Castor oil were received from Loba Chemie. The chemicals were used as received.

Synthesis of diazotised p- Chloro Aniline cardanol- formaldehyde resin (CH)

5.5 g of diazotised p- Chloro Aniline cardanol dye was condensed with 4 ml of formaldehyde and 3 ml of 3N. H₂SO₄. The reaction was carried out at 100°C for 6 hours. A dark red brown colored solid diazotised p- Chloro Aniline cardanol formaldehyde resin (CH) obtained.

Synthesis of Castor Oil Based Polyurethane (PU)

0.932 g of Castor Oil was allowed to react with 0.52 g of toluene diisocyanate (TDI) to maintain the NCO/OH molar ratio at 2.0. The reaction was carried out in a small beaker at about 45°C in methyl ethyl ketone (MEK) with constant stirring for 45 min until a viscous prepolymer of pale yellow color polyurethane separated out. In a similar way 0.470 g and 0.417 g of toluene diisocyanate to maintain NCO/OH molar ratios at 1.8 and 1.6 respectively.

Synthesis of Interpenetrating Polymer Network (IPN)

The polyurethane (PU) and diazotized cardanol- formaldehyde (CH) with a constant PU/CH weight – to – weight ratio (50 : 50) for different NCO/OH molar ratios were separately taken in MEK in a reaction vessel in presence of benzoyl peroxide (BPO) and ethylene glycol dimethacrylate (EGDM). The mixture was constantly stirred at room temperature by means of a magnetic stirrer for 15 min to get a homogeneous solution and thereafter the temperature was raised to 75°C to initiate the polymerisation and stirring was continued for about 1 h to get a viscous mass which was poured into a glass mould and kept in a preheated oven at 75°C for 24 h. The thin film thus formed was cooled and removed from the mould and labelled. The well cured polyurethanes were subjected to ageing studies. The feed composition data of IPNs are furnished in the Table-1

TABLE – 1 FEED COMPOSITION DATA OF IPNs

Sample Code	NCO/OH mole Ratio	PU:CH Weight Ratio
IPN-1	2	50:50
IPN-2	1.8	50:50
IPN-3	1.6	50:50

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° ± 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 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 2: Weight loss of polyurethanes based on diazotized cardanol- formaldehyde resins in different chemical environment

Sample Code	Water	Ethanol	NaCl	1N HCl	1N NaOH	30% H2O2	Diethyl ether	Toluene	DMA
IPN-1	0	0	0	0	0	0	0	0	+87.4
IPN-2	0	0	0	0.17	0.28	0.21	0	1.42	+90.6
IPN-3	0	0	0	0.20	0.36	0.32	0	1.98	+94.3

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 diazotized cardanol-formaldehyde resins under hydrolytic conditions. Hence all the synthesized polyurethanes are found to possess very good hydrolytic stability (Table 2). 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 2), it has been found that IPN-1 stable towards acid, base and oxidant. But in the case of IPN-2 & IPN-3 in acidic and basic medium, weight loss ranges from 0.17-0.36. In the case of oxidant the percentage of weight loss found to be 0.21&0.32. The hydrolytic degradation of the IPN-2& IPN-3 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.

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. But in toluene the percentage of weight loss for IPN-2 & IPN-3 are found to be 1.42 & 1.98. 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 95% (Table 2). 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. But a small change in thickness (about 0.75%) in the case of IPN-3 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 - 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 IPN-1 & IPN-2. But shore-A hardness increases to about 1.20% in the case of IPN-1 and 1.23% in the case of IPN-2. The IPN-3 resins showed 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 microorganisms 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].

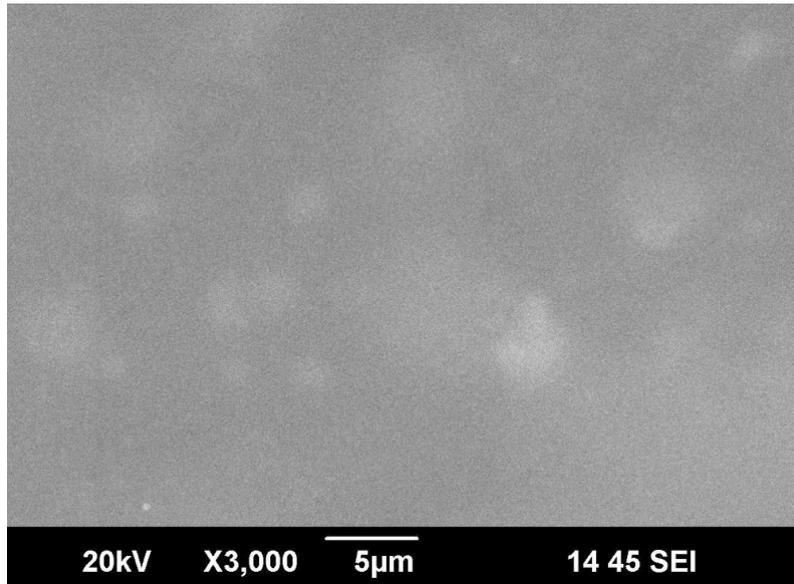


Figure 1. SEM photograph of IPN-1 (before soil burial test)

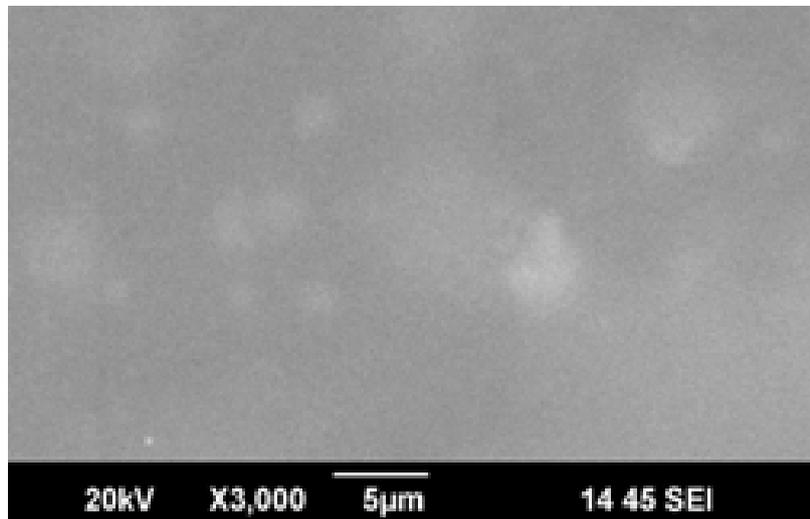


Figure 2. SEM photograph of IPN-1 (after soil burial test)

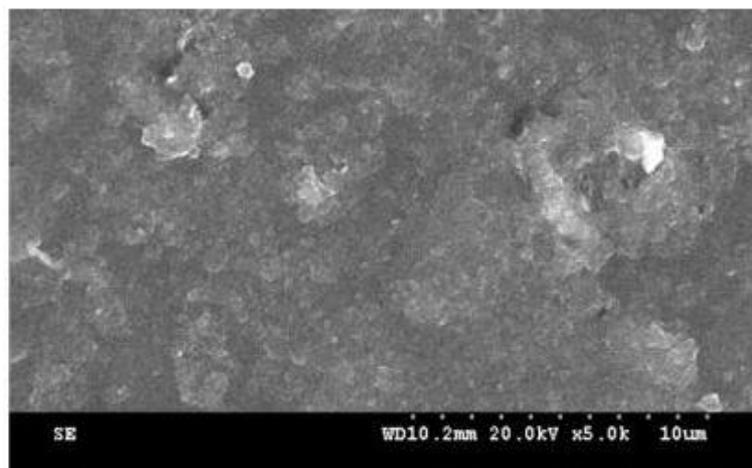


Figure 3. SEM photograph of IPN-3 (before soil burial test)

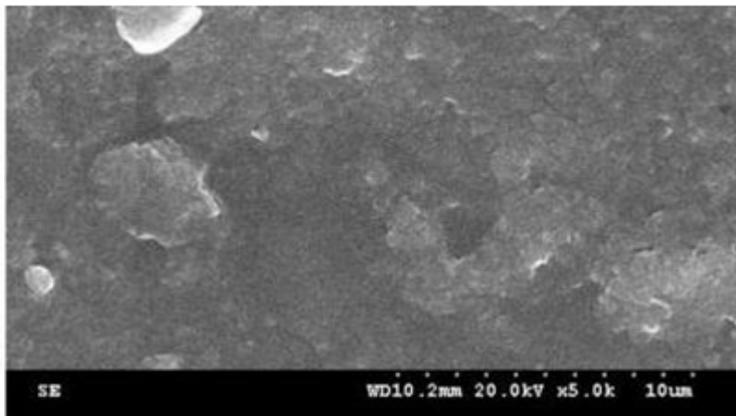


Figure 4. SEM photograph of IPN-3 (after soil burial test)

In the present study, the environmental resistance of the synthesized 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 IPN-1 is more stable than the corresponding IPN-2 & IPN-3 polyurethanes. All the polyurethanes exhibit very good hydrolytic stability. The IPN-1 is thermally and dimensionally more stable and having more resistivity towards acid, base and oxidizing agent. But the IPN-2 & IPN-3 are 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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