A Novel Biodegradable Polymer: Synthesis and Applications

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Abstract:

The transition from conventional polymer to biodegradable polymer is getting importance day by day. This paper discusses the synthesis and characterization of a non toxic, biocompatible novel polymer. The insertion of a hydrolysable moiety in the polymeric chain greatly enhanced the biodegradation of the polymer in environment experimentally verified by soil burial test. The polymer so synthesized has been characterized by IR Spectrophotometric analysis , XRD analysis , hydrolytic stability test, soil burial test. Mechanical properties and thermal properties have also been explored.

Keywords: Biodegradable polymer, synthesis, characterization, application, use.

1. Introduction

The huge and multifaceted use of polymer materials in almost every field of human life is causing havoc to the living organisms and mankind due to its accumulation in fields , ocean and environmental at large. As most of them used are non biodegradable they remain intact for years interfering with various natural processes. Essentially disposal of polymeric waste is the biggest cause of concern in the 21st century. Incineration is one available option that causes again environmental pollution. Recycling essentially is a very good option though its application is only limited. In this regard the use of biodegradable polymer is increasing by the day. Apart from commodity materials required in bulk amounts speciality applications are gaining popularity much in the last decades. Biodegradable polymers after use get back into the environment as non toxic and biocompatible, compounds [1].Biodegradable polymers are also widely being used in biomedical; applications such as controlled release of drugs and drug delivery, disposable sutures, in biodegradable polymeric scaffolds and tissue engineering, biodegradable hydrogels [2].

A wide range of people is affected by the many application of polymeric drug delivery systems. Cardiac patients (nitroglycerin), diabetics (insulin), cancer patients (chemotherapeutic drugs), and women (progesterone) are just few of those affected by drug delivery systems using polymers [3]. The biodegradable polymers are tested for their biodegradability by soil burial test and bacterial actions on the biodegradable polymers and monitoring by IR spectroscopy [4].

Lactic acid is a well-known monomer used extensively for the synthesis of biodegradable polymer for biomedical application [5]. But poly (lactic acid) thus prepared is brittle in nature. So people were attracted to copolymers of lactic acid(LA) as well as other polymers having potential biomedical applications. Fukuzaki et al. synthesized copoly (lactic acid/aromatic hydroxy acids) [6]. They produced biodegradable copolyesters

having aromatic rings ($C_6H_5CH_2.C_6H_5$) as side chain residues, e.g., LA/L-3-phenyllactic acid was synthesized by direct copolycondensation without catalyst at 200°C.

Lot of works has been done with aliphatic polyesters. Novel regular network polyesters were prepared from pentaerythritol and aliphatic dicarboxylic acids of different numbers of methylene groups. Prepolymer prepared by melt polycondensation was cast from dimethylformamide solution and post polymerized at 270°C for various times to form a network. The resultant films were transparent and flexible. The network polyesters obtained were characterized by infrared absorption spectra, wide-angle X- ray diffraction analysis, density, DSC, tensile test and alkali hydrolysis [7].

Hydroxy terminated poly (hydroxy alkanoates) (PHA) have also come up with various applications. PHAs are generally biodegradable plastics and posses properties ranging from those of elastomers to thermoplastics and thermosets [8].

Abraham J. Domb synthesized biodegradable aromatic anhydride copolymers. The aromatie copolyanhydrides based on the common diacids isophthalic acid (IPA), terephthalic acid (TA), 1,3-bis (p-carboxyphenoxy) propane (CPP) and fumaric acid were synthesized and characterized. They are used as drug delivery system [9].

Novel biodegradable poly (hydroxyalkylene carbonates) (PHAC's) which are a versatile class of polymers for medical and pharmaceutical applications were first prepared by Murat Acemoglu et al. The PHAC's are the first examples of water soluble polycarbonates. Due to water solubility, these polycarbonates may replace PEG's in some applications [10].

Works have also been done with poly (organophosphazenes). Allock et al. synthesized four different poly (organophosphazenes) bearing esters of glycolic or lactic acid as side groups in order to investigate their stability in aqueous media. The polymers glycolato) phosphazene], poly[bis(benzyl poly[bis(ethyl glycolato)phosphazene] are poly [bis(ethyl lactato)phosphazene], and poly[bis(benzyl lactato)phosphazene]. The objective of this work was to design and develop synthesis of the materials that might behave like poly(glycolic acid) (PGA) and poly(lactic acid) (PLA) but have unique combination of properties. However, unlike PGA and PLA these polymers are not crystalline. They hydrolyze at a faster rate than either PGA or PLA. The lack of crystallinity and rapid hydrolysis rate may be appropriate for controlled drug release applications [11].

Later people were attracted to e-caprolactone, which is readily available from petrochemical sources and easily converted into high molecular weight chains by organometallic catalysts. Poly (e-caprolactone), which readily crystallizes, is known for its unique set of properties, including biocompatibility, biodegradability.

Biodegradable polyurethanes now a days are having constantly growing attention. This is because their properties can be tailored by variation of their ractive components: the diol chain extender, the flexible polyols, and the polyisocyanate. Polyurethanes are the most important polymers used in biomedical devices. Presently, over 35 million pounds are being consumed in this area and rapid growth is expected [12]. A thermoplastic poly (ester -urethane) was synthesized using stannous octoate as catalyst, followed by an increase in molecular weight through urethane linkage. The use of I, 4- butanediol results in oligomer molecules with hydroxyl functionality at both the ends. It was found to be amorphous with Te varying from 53 to -45°C. Mechanical testing and hydrolytic degradation was carried out in different medium [13].

Hironbu Fukuzaki and others synthesized low molecular weight copolymers of lactic acid and e-caprolactone by direct copolymerization at 200°C under nitrogen atmosphere [14]. The in vivo degradation was studied in buffer solution with and without enzymes.

In one study, a lactic acid based telechelic prepolymer with hydroxyl groups at the ends was prepared which can be used as a diol for polyurethane preparation. Lactic acid was esterified with I, 4- butanediol in presence of tin octoate as catalyst. The glass transition temperature was varied from 16.7 to 46°C [15].

Attempts were made to synthesize completely nontoxic bioabsorbable polyurethane and can be synthesized if the urethane segments hydrolyze completely into biocompatible degradation products. For example, L-lysine diisocyanate(LDI) hydrolyzes into ethanol and L-lysine, which are biocompatible. R.F. Storey and others synthesized biodegradable poly (ester-urethane) networks from ethyl 2, 6-diisocyanato hexanoate (L- lysine diisocyanate) (LDI) and a series of polyester triols. Polyester triols were synthesized from D, L-lactide, e-caprolactone using glycerol as initiator and stannous octoate as catalyst. Polyurethane networks were cured using [NCO:OH]=1.05 and stannous octoate [.05 wt%] for 24 hours at room temperature and normal pressure. LDI based polyurethane network was totally amorphous. Networks based on poly (D, L-lactide) triols were rigid (T$_2$= 60°C) with ultimate tensile strength of 40-70 MPa, tensile moduli of -1.2-2 G Pa, and ultimate elongations of ~4-10%. Networks based on e- caprolacone triols were low molecular elastomers with tensile strength and moduli of-1-4 MPa and ~3-6GPa, respectively, and ultimate elongations of ~50-300%. Hydrolytic degradation under simulated physiological conditions showed that D. L-lactide based homopolymer networks were the most resistant to degradation, undergoing no virtual change in mass and physical properties for 60 days. E-Caprolactone based networks suffered substantial losses in physical properties after only 3 days [16].

A high molecular weight esterdiol still cannot be obtained easily. Efforts were made in this regard and polyester with high number-average molecular weight (M>30,000) was prepared. Then it was reacted with diisocyanate. Polyester was first synthesized by condensation of dimethyl succinate [DMS] with 1,4-butanediol [BD] using various metal alkoxides as catalysts. Second step was the chain extension with hexamethylene diisocyanate as chain extender. Using different enzymes degradation was studied. The enzymatic degradation of chain extended polyester was slightly lower than before chain extension, but proceeded steadily [17].

The most popular biodegradable polymers which are used for biomedical applications (PLA, PGA,poly(ε-caprolactone) and their co- and terpolymers) are generally semicrystalline, and they lead to heterogenous degradation patterns, i.e., the amorphous region tend to degrade first. This can be a disadvantage as the degradation rate is typically not linear with weight loss and quite often a catastrophic loss in strength is observed with loss in weight. As an alternative to this, difunctional hydroxy terminated poly (ε-caprolactone-co-δ-valerolactone) (PCV) oligomers were synthesized by the diol-initiated bulk copolymerization of e-caprolactone and δ- valerolactone. Then it was reacted with triphenylmethane triisocyanate. Completely amorphous network resulted [18].

Ethics Approval: This work is purely carried out in the laboratory of IIT kharagpur by myself and has not been published in any other journals.

2. Materials

The following materials were used in the present investigation after necessary purification as per standard laboratory procedure.

1. Lactic Acid (LA), Quest chemicals, India.

2. Polyethyleneglycol-200 (PEG-200), E.Merk, India.

3. Dibutyltindilaurate (DBTDL), Fluka (used without purification)

4. Toluenediisocyanate (TDI), E.Merk, Germany (used as received)

5. Tetrahydrofuran (THF), E.Merk, India.

6. Sodium hydroxide pellete, Quligens, India.

7. Benzene, Quest chemicals, India.

8. Toluene, Quest chemicals, India.

9. Sodium Chloride, E, Merk.

3. Experimental Procedure

3.1 Synthesis of the Esterdiol

The esterdiol was synthesized by reacting lactic acid (LA) with PEG-200 in benzene in presence of DBTDL as catalyst. The esterification reaction is extremely slow and towards the end of the reaction the reaction become even slower. So employing a large amount of time and driving out water from the reaction mixture, which is byproduct of the reaction, by Dean Stark apparatus the reaction was driven to the right side. Also the diol (PEG- 200) was taken in excess..

In a round bottom flask LA and PEG-200 were taken in 1:2 molar proportion. Benzene was added in such a manner so as to have a 50 weight percent of the reagents. Catalyst DBTDL was added (1 wt.% to the total amount of reactants). To the mouth of the reaction vessel a Dean Sterk apparatus was fitted. The reaction mixture was refluxed for 16 hours at 80°C after fitting a reflux condenser over the Dean Stark apparatus.

3.2   Purification and Collection of the Ester

In the synthesized polyethylene lactate ester-diol some amount of unreacted lactic acid, PEG-200 and benzene were present. The low boiling solvent and unreacted reagents were removed by fractional distillation. The last fraction, which is the ester-diol, was collected by vacuum distillation. The polyethylene lactate ester diol is a colourless transparent viscous liquid.

3.3   Synthesis of Polyurethane

Polyurethane was synthesized by reacting the ester diol with TDI in various molar proportions (NCO/OH=2.0 and 2.25) using excess of isocyanate taken in dry THF (50 wt.% of the reactants) in presence of DBTDL (.05 wt.%) as catalyst. This polyurethane synthesis was carried out in a round bottom flask with a reflux condenser and thermometer pocket in a dry environment. This reaction is a highly exothermic reaction; hence THF solvent was as used heat transfer medium, which removed the exothermic heat to the condenser during refluxing. If there is no proper heat transfer system then the excess heat produced by the system will deteriorate the product quality. The reaction was continued at 80°C temperature for two hours. Then by applying vacuum the excess solvent present in the reaction mixture was removed. The product of the reaction was a high viscous polyurethane prepolymer. This polyurethane was cast on a Teflon surface to make polyurethane thin sheet.

3.4   Casting and Curing of Polyurethane Sheet

During the casting of prepolyurethane on Teflon sheet there arises a problem of bubble formation. This bubble is produced due to the liberation of CO_2 during and moisture curing of the prepolyurethane. Trapped air bubbles in the viscous mass also produce bubble. To avoid this viscosity was maintained at such a level that the bubble formation could be eliminated. Excess solvent before casting causes delayed curing but more viscous. prepolymer causes more bubble formation tendency. So the viscosity of the prepolymer was adjusted by trial and error method. Then that prepolymer was cast on a Teflon sheet. The polyurethane sheet obtained, as cast sheet was moisture cured for 24 hours at room temperature. This cured sheet was then taken for various subsequent analysis and testing.

3.5   Density and Physical Properties

The density of the polyurethane samples was determined with the help of a pycnometer. Density is required for the calculation of specific tensile strength.

3.6   IR Study

For structural analysis the IR spectrum of the PU sample was done using Perkin Elmer spectrophotometer, model no.883. For the IR experiment the polyurethane prepolymer was used to make a film on a glass plate. This film was kept at room temperature for 24 hours for moisture curing. The cured film was then removed from glass plate by dipping in hot water. Then that film was cleaned thoroughly with acetone and was kept in vacuum desiccator for 24 hours. This conditioned film was used for IR analysis. The IR spectrum was taken for the frequency range of 200-4000 cm.

3.7   XRD Study

To know whether prepared PU is crystalline or amorphous the X- ray diffraction study was done.

The sample was prepared and conditioned as done for IR analysis. The XRD study was done using Phillips, Holland, and model no. PW 1729 XRD Analyzer for the range 20-10°-40° using CuKo as target.

3.8   Test of Mechanical Properties

For testing of mechanical properties the sample was prepared by the following method. The prepolymer after moisture curing was kept in a vacuum desiccator overnight. Then it was cut into standard dumbbell test specimen using a die-punch cutter. Then that dumbbell specimen was subjected to test for various mechanical properties like tensile strength, elongation at break and modulus using KMI Tensile Testing machine at a cross head separation speed of 500 mm/ min.

3.9   Test for Hydrolytic Stability of the Synthesized Polyurethane

3.9.1   Hydrolytic Stability in Water

A pre weighed conditioned polyurethane sample was kept immersed in a conical flask containing distilled water at room temperature. Then after different time interval the sample was taken out, wiped out with blotting paper, kept overnight in vacuum desiccators and weighed within a previously weighed weighing bottle. Thus the change in weight was noted.

3.9.2   Hydrolytic Stability in Mineral Acids

Previously weighed PU samples were kept immersed in 10% HCL, 10% H2SO4, 10% HNO3. After certain time intervals they were taken out, washed with water and kept in vacuum desiccators. Then they were again weighed. Weight changes were noted.

3.9.3   Stability in Aqueous Alkali Solution

For this experiment the sample was prepared as that for mineral acid test. Then the PU sample was dipped in alkali solution. After certain time intervals sample was taken out, washed and dried as before and the change in weight was recorded.

3.9.4   Stability in 10% NaCl Solution.

Stability of the prepared PU sample was measured in 10% NaCl solution also. The conditioned PU sample was immersed in 10% NaCl solution at room temperature and after different time intervals the samples were taken out, washed thoroughly in distilled water, dried as before. Change in weight was recorded.

3.10   Solvent Resistance

The solvent resistance property of the polyurethane was tested in different solvents like toluene, chloroform and tetrahydrofuran at room temperature. In order to investigate the solvent resistance, all the prepared samples of known weight were kept immersed in the solvents in stoppered conical flasks for certain

periods. Weight change of the samples was measured by taking out the specimens from the solvents followed by wiping out the solvent film by blotting paper and the specimens were placed inside a preweighed weighing bottle and weighed.

3.11   Soil Burial Test

In order to perform soil burial test soil was collected in a pot from the garden of Materials Science Center; IIT Kharagpur. Then the soil was digged. A polymer film (previously weighed), was kept inside the soil after taking a photograph. After 14 days it was taken out from the soil, washed thoroughly with distilled water, dried and kept in a vacuum desiccator. Then weight los was measured. Photograph of the degraded film was again taken.

3.12   Thermal Properties Of The Polyurethane DSCITGA analysis of the polyurethane

The cast polyurethane sheet after curing was kept in a vacuum desiccator for overnight. Then a small portion of it was used for DSC analysis.

The DSC analysis was performed in a DSC analyzer (Stantan Redcroft) in nitrogen atmosphere. Heating rate was 10°C/min.

4.1 Synthesis of Poly (ester urethane)

The main objective of this investigation was to design and synthesize novel biodegradable polyurethane. For this purpose inclusion of ester linkage in the polyurethane backbone was thought of. It is obvious that the extent and rate of biodegradation could be governed by the frequency of the biodegradable ester linkages in the polyurethane chain. In view of this we selected lactic acid and low molecular weight PEG (PEG-200) for making low molecular weight hydroxy terminated ester (ester diol). The synthesis reaction of the esterdiol is shown in schemel. Such ester diol was used for synthesis of polyurethane by reaction with 2,4-toluenediisocyanate (TDI) at various molar proportions. Here in this synthesis if the ratio between NCO and OH is kept at 2.5 or above the polymer produced becomes brittle in nature and if the same is kept below 1.5 the prepolymer becomes very low viscous. So it requires an adjustment of the mole ratio of NCO with OH so that the polymer neither becomes brittle nor sticky in nature.

In this investigation the polymer was synthesized by taking two different stoichiometric ratios of NCO/OH. The ratios were 2:1 and 2.25:1. The lactic acid and PEG based polyurethane was synthesized in two steps. In the first step the ester diol was synthesized by reacting lactic acid with PEG- 200. One hydroxyl group of PEG-200 was reacted with the carboxyl group of lactic acid to form the polyethylene lactate leaving two unreacted hydroxyl groups. There might be a self-condensation of lactic acid but keeping a higher proportion of PEG it was greatly minimized.

The esterification reaction was continued at reflux temperature of benzene in presence of DBTDL as catalyst for 15 hours. The esterification

was facilitated by removing water as azeotrope with benzene with the help of Dean and Stark apparatus.
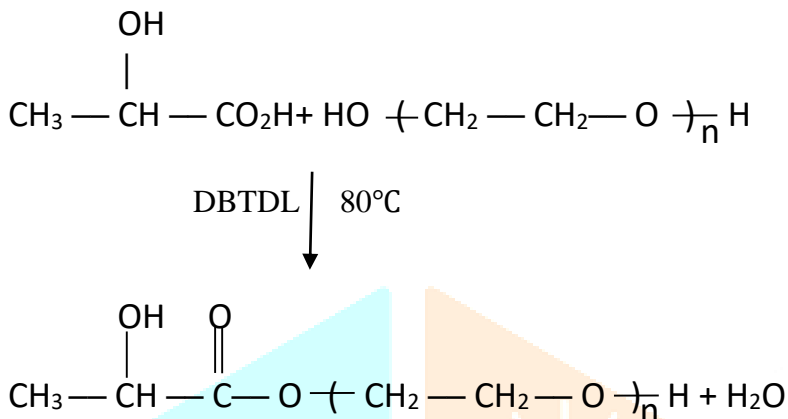
Pure polyethylene glycol lactate was obtained through fractional distillation to remove the unreacted lactic acid and PEG-200 followed by vacuum distillation of the remaining liquid in the distilling flux. Polyethylene glycol lactate was collected as a colorless viscous liquid at room temperature.

In the next step the ester diol was reacted with 2,4- toluenediisocyanate in dry THF medium at 80°C with DBTDL as catalyst. The reaction was continued for 2 hours to obtain a viscous solution of PEG lactate-based polyurethane in THF. Two different polyurethanes were obtained by using ester diol: TDI mole ratios of 2.2 and 2.25. Below and above these diol : TDI mole ratios resulted useless polyurethane products.
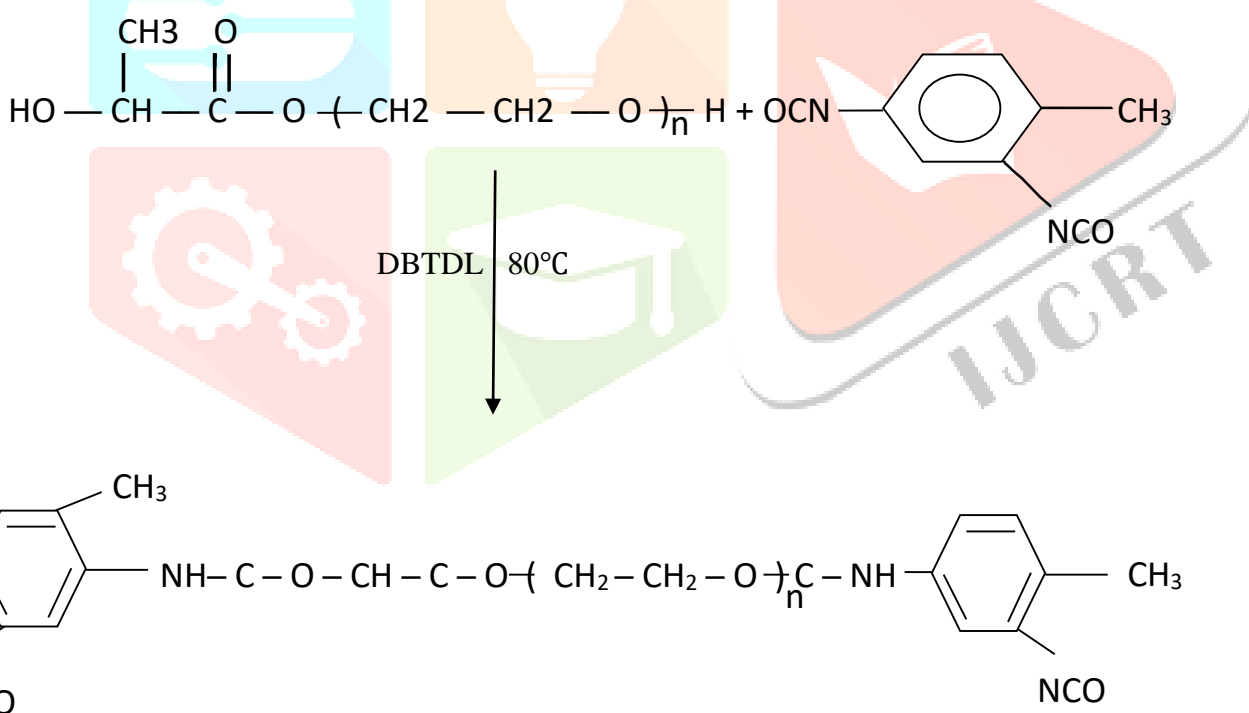
Casting of polyurethane sheet from viscous solution is a rather tricky process. Before casting of polyurethane sheets the major THF was removed by applying vacuum to avoid bubble formation after casting due to solvent evaporation and simultaneous curing by atmospheric moisture. The thickness of the cast sheet also has a role in avoiding bubble formation. Beyond the 1-1.5 mm thickness of the sheet the possibility of bubble formation is more. So the viscosity / consistency of the polyurethane solution was maintained at such a level by applying vacuum that the thickness of the sheet did not exceed 1-1.5mm.

4.2 Scheme 1: Synthesis of ester- diol and polyurethance
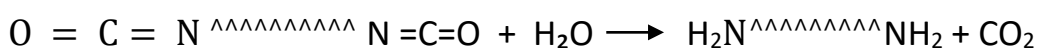
Step 1: Reaction of LA with PEG

$$CH_3 - \underset{\underset{OH}{|}}{CH} - CO_2H + HO -(CH_2 - CH_2 - O)_n H$$

DBTDL | 80°C

$$CH_3 - \underset{\underset{OH}{|}}{CH} - \underset{\overset{O}{||}}{C} - O -(CH_2 - CH_2 - O)_n H + H_2O$$

Step 2 Reaction of esterdiol with TDI (excess)

$$HO - \underset{\underset{CH3}{|}}{CH} - \underset{\overset{O}{||}}{C} - O -(CH2 - CH2 - O)_n H + OCN - \underset{}{\bigcirc} - CH_3$$
NCO

DBTDL | 80°C

$$CH_3 ... NH - C - O - CH - C - O-(CH_2 - CH_2 - O)_n C - NH - \bigcirc - CH_3$$
NCO   NCO
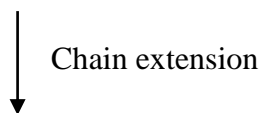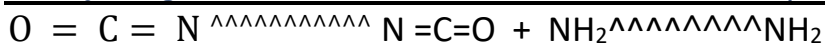
4.3 Curing of Polyurethane

The curing of the polyurethane was effected in two steps: In the first step the sheet was allowed to slow evaporate the residual solvent in the sheet with simultaneous curing reaction in presence of atmospheric moisture for 24 hours. The sequence of probable reactions during curing are shown below:

$$O = C = N \, ^{\wedge\wedge\wedge\wedge\wedge\wedge\wedge\wedge\wedge} N = C = O + H_2O \longrightarrow H_2N ^{\wedge\wedge\wedge\wedge\wedge\wedge\wedge\wedge} NH_2 + CO_2$$

[A]

O = C = N ^^^^^^^^^^ N =C=O + NH₂^^^^^^^^NH₂

Chain extension

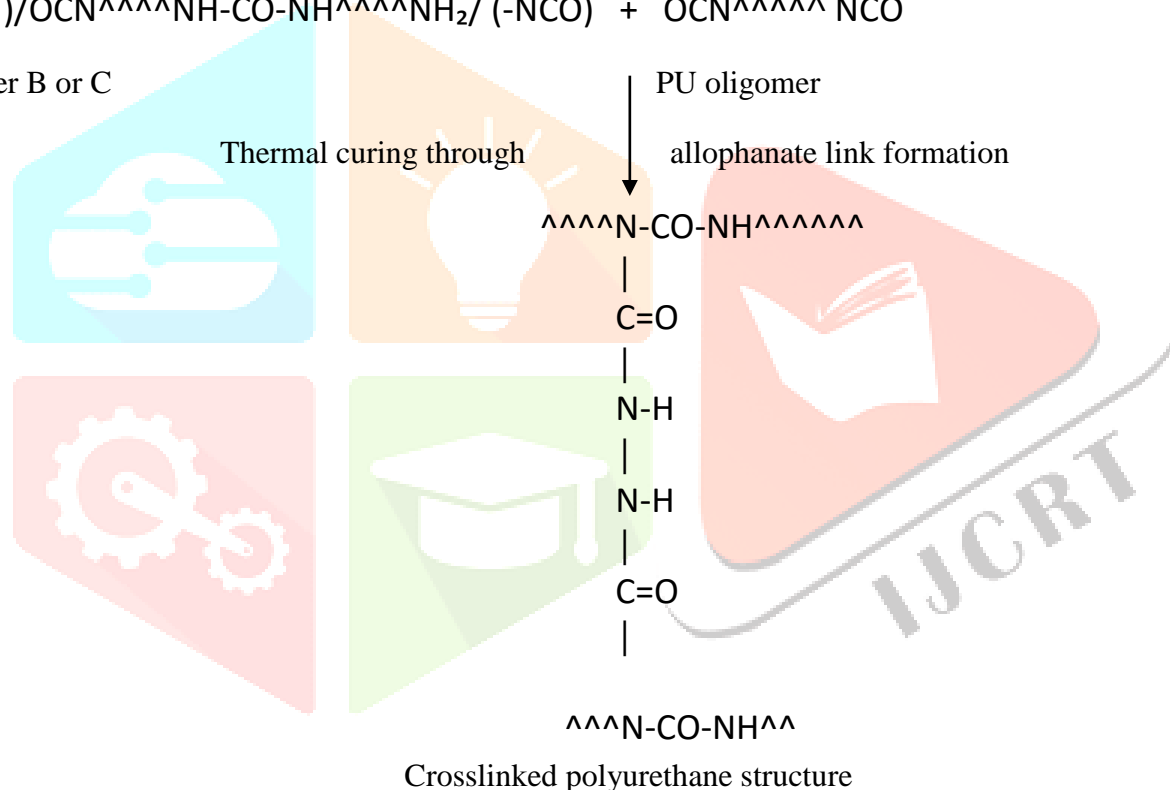OCN^^^ NH-CO-NH^^^NH₂ or OCN^^^NH-CO-NH^^^NH-CO-NH^^^NCO

[B] [C]

The concentration and the rates of formation of the intermediates A, B and C etc. will be dependent on the moisture concentration and the concentration of the NCO terminated PU oligomer.

The polyurea structures B and C so formed will participate in the crosslinked polyurethane structure as shown below:

(H₂N)/OCN^^^^NH-CO-NH^^^^NH₂/ (-NCO) + OCN^^^^^ NCO

Either B or C   PU oligomer

Thermal curing through   allophanate link formation

^^^^N-CO-NH^^^^^^
|
C=O
|
N-H
|
N-H
|
C=O
|
^^^N-CO-NH^^

Crosslinked polyurethane structure

4.4 Measurement of Density

The composition density and physical appearance of the synthesized and ed polyurethane are shown in Table 1. It is observed that as the ratio of nate and diol increases the density of the polyurethane increases. It is ur to the fact that as the ratio of isocyanate to diol increases the amount of paywethane hard segment increases in the polymer structure. Increase in sad segment causes more hard segmental alignment and enhance density. The appearance of the polymer was light yellow in color. This may be due to the generation of some chromophoric groups during synthesia.

4.5 IR Analysis

To ascertain the formation of ester-diol by the reaction of lactic acid witch PEG-200 IR spectroscopic analysis was carried out. Pure ester-diol was obtained by fractional distillation of crude ester-diol having benzene and unreacted excess PEG-200 followed by vacuum distillation. The IR spectroscopy of esterdiol and the cured

polyurethane shown in figures 1 and 2 respectively. The assignment of various peaks of the estes is given in Table 2. The peaks at 1735 cm³, 1249 cm' and 1122 cm confirm the exter linkage.

The assigned peaks for polyurethane are given in Table 3. The peaks at 3483 cm³, 1689 cm indicates urethane linkage in the polymer. The IR spectroscopy may be used as an important tool for monitoring the curing reaction of polyurethane to ascertain the intermediate structures. This may

further ensure the elucidation of curing reaction mechanism of polyurethane. In this present investigation such study could not be made due to lack of time and easy access to an IR spectrometer.

4.6 XRD Analysis of the Polyurethane

In order to get an idea on the morphological picture of the synthesized polyurethane, X-ray diffraction analysis was carried out. The X-ray diffraction patterns of the polyurethanes are shown in Figures 3 and 4. In Figure 3 the PU2.0 shows two humps at 20-21.77° and 12° and in figure4 the PU2.25 shows two humps at 20=21.75° and 12.38°.

From the XRD patterns presented in the figures it appears that both the composition of the polyurethanes synthesized are amorphous in nature. Although the polyurethane contains hard segments but due to lack of proper alignment of the molecules crystalline phase was not formed. This happened due to easy onset of crosslinking formation between the segments of the molecules. Not only this molecular orientation was hindered on the airside of the cast due to rapid solvent evaporation and moisture curing. If such reactions could be avoided during moisture curing inter-segmental alignment would have been possible to develop crystalline phase in the polymer matrix. Such process would have a tremendous influence on the one mechanical properties of the polyurethane synthesized.

4.7 Mechanical Properties

Evaluation of the mechanical properties of polyurethane is essential since any device made up of this polyurethane must have adequate strength and dimensional stability. Such mechanical characteristic is highly dependent on the molecular weight of the synthesized product. So measurement of mechanical strength can help altering the molecular weight by manipulation in the reactants mole ratio and polymerization condition. The mechanical properties of the synthesized polyurethane like tensile strength, elongation at break have been measured and the results are shown in table 4. In the morphology of the polyurethane, it is seen that there are two types of domains presents. One is hard domain, which is formed by the aromatic isocyanate group, and another is the soft domain formed by the polyol.

So, as the isocyanate to diol ratio increases the hard domain increases and the amount of hydrogen bonding between the urethane linkages also increases. Hence, the tensile strength of the polymer increases with the increasing isocyanate to diol ratio.

But the elongation at break decreases with the increase in tensile strength. It is due to the fact that with increasing isocyanate to diol ratio the amount of hydrogen between the urethane linkages increases and cross linking also increases. As a result the polymer becomes more stiff and it losses its elastomeric property. Hence, the elongation at break decreases with increasing the isocyanate to diol ratio.

4.8 Thermal Properties of the Polymer

DSC/TGA Analysis

For evaluating the thermal stability of the synthesized polyurethanes, thermogravimetric analysis and differential scanning calorimetric analysis were carried out in nitrogen atmosphere at a heating rate of 10°C/minute. The results of the DSC/TGA analysis are shown in Table 5 and figures 5 and 6.

In both the polyurethanes the first weight loss occurs from 157 to 234°C. But this weight loss is not due to thermal degradation of the polymer. It is due to the vaporization of the trapped solvent and oligomeric component in the polyurethane.

The actual weight loss occurs at three steps for both the sets. This is due to the thermal degradation of the polymer. From the data in Table 5 it is seen that maximum weight loss of both the polymers occurs in the temperature range 227-369°C. So it may be said that the synthesized polyurethane is stable upto about 225°C,ie, any device made of such polyurethane safely used upto 150°C. Such high thermal stability of the polyurethane may be attributed to the higher concentration of the hard segments as well as to the presence of aromatic ring in the polymer backbone.

4.9.1 Hydrolytic Stability

The polymer shows systematic loss in weight in mineral acids. Among the acids highest loss in weight is observed in nitric acid. This is due to the faster oxidative degradation of the urethane linkages by small and strong nitrate ion.

4.9.2 Stability in Aqueous Alkali Solution

When immersed in alkali solution the polymer shows large loss in weight. This is due to the fact that alkali reacts vigorously with the ester group present in the polymer. The loss in weight with time in dilute alkali solution is given in table 8.

4.9.3 Stability in 10% NaCl Solution

The polymer is to some extent stable in saline water. But if kept immersed for long time it swells and a gradual gain in weight is observed (table 9).

4.10. Solvent Resistance of The Polymer

The extent of swelling of the polymer in chloroform, toluene and tetrahydrofuran is shown in Table 10. The amount of swelling is least in toluene and highest in tetrahydrofuran. This is due to the polar characteristics of the solvents. Since polyurethane is polar so polar-polar interaction will favor the penetration of the solvent in the bulk of the polymer system studied.

4.11 Soil Burial Test of The Polymer

From the photograph of the polymer sample it is seen that the surface of the polymer eroded substantially. A marked change in weight is also seen from Table 11.
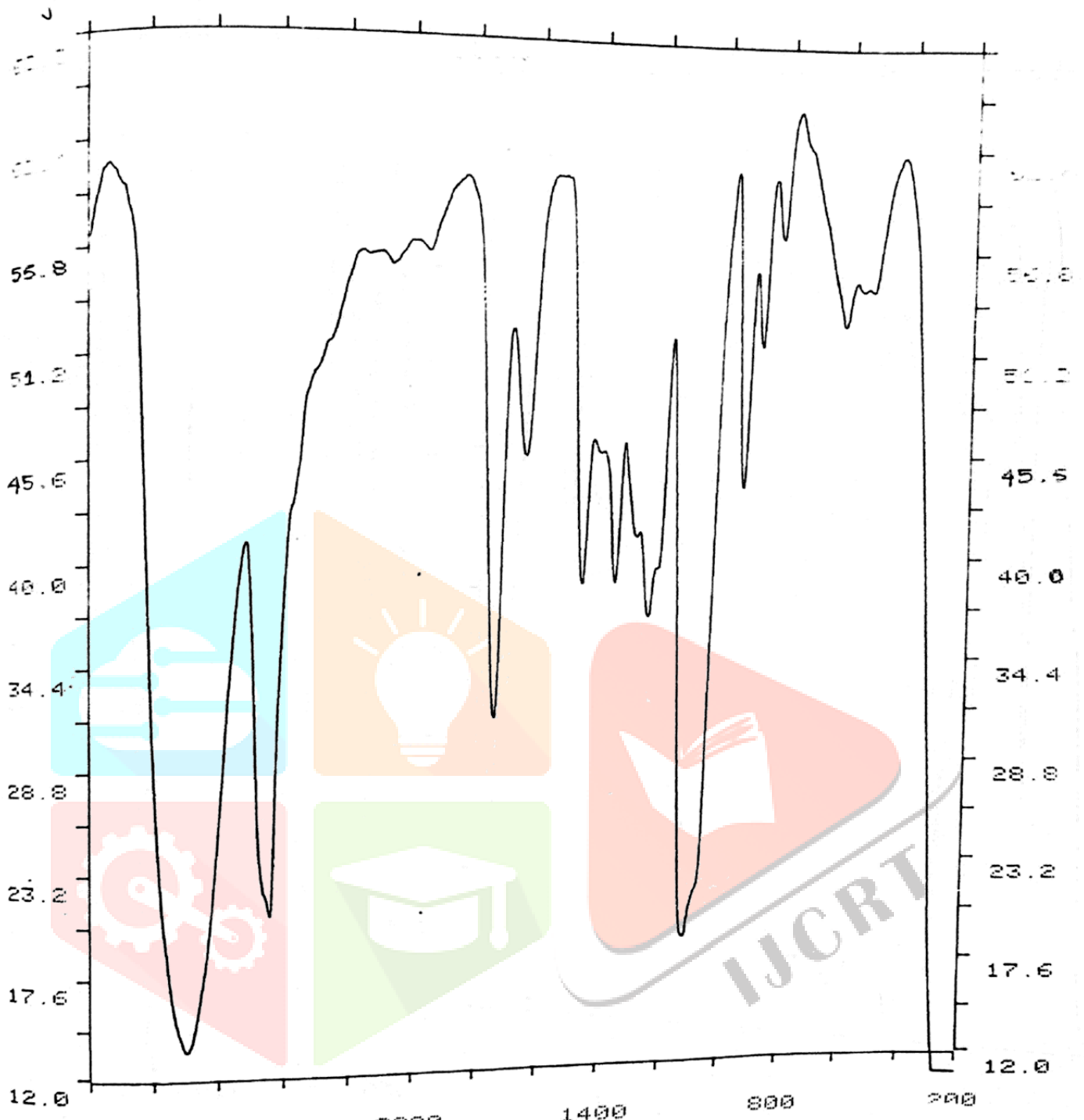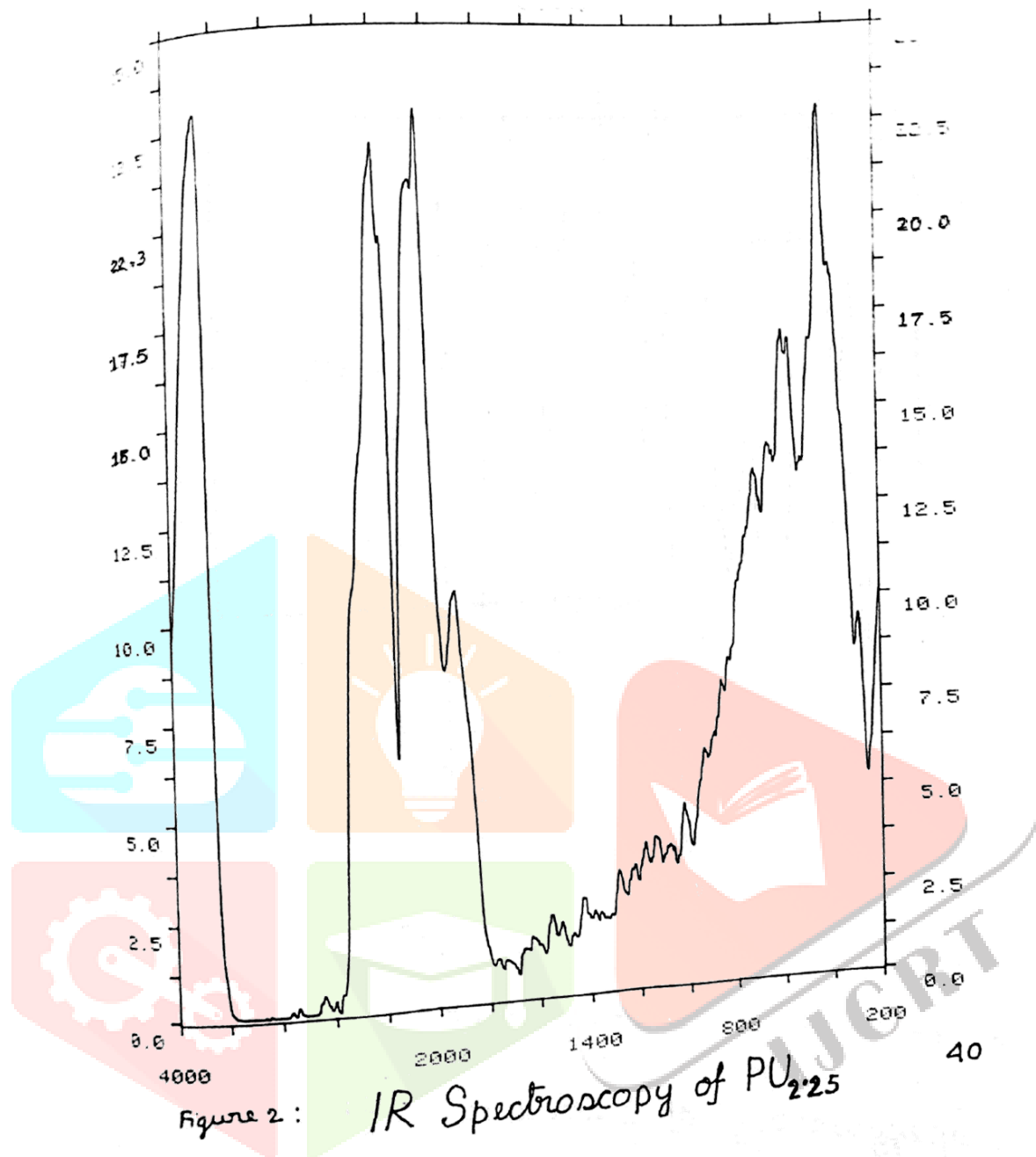
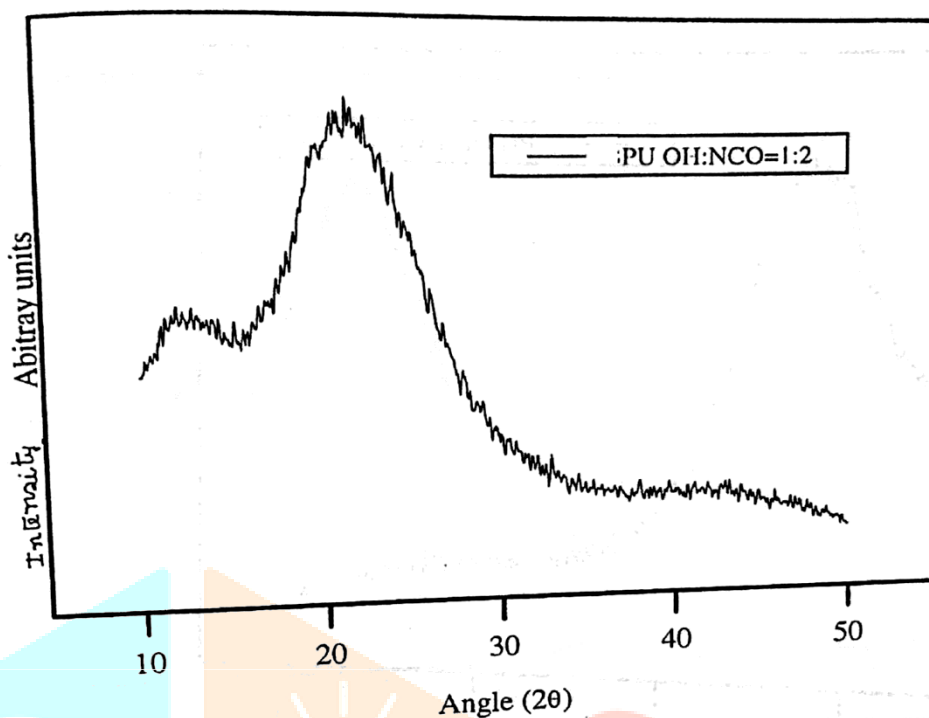Figure 1 : IR Spectroscopy of Ester diol

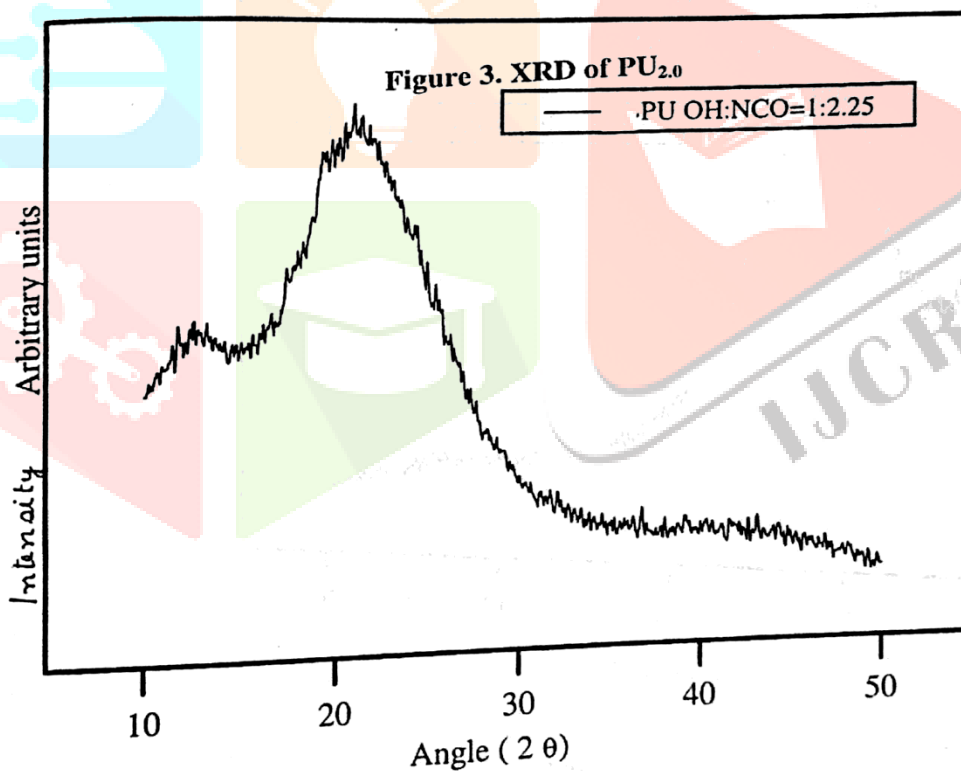Figure 2: IR Spectroscopy of PU$_{2.25}$

Figure 3. XRD of PU$_{2.0}$
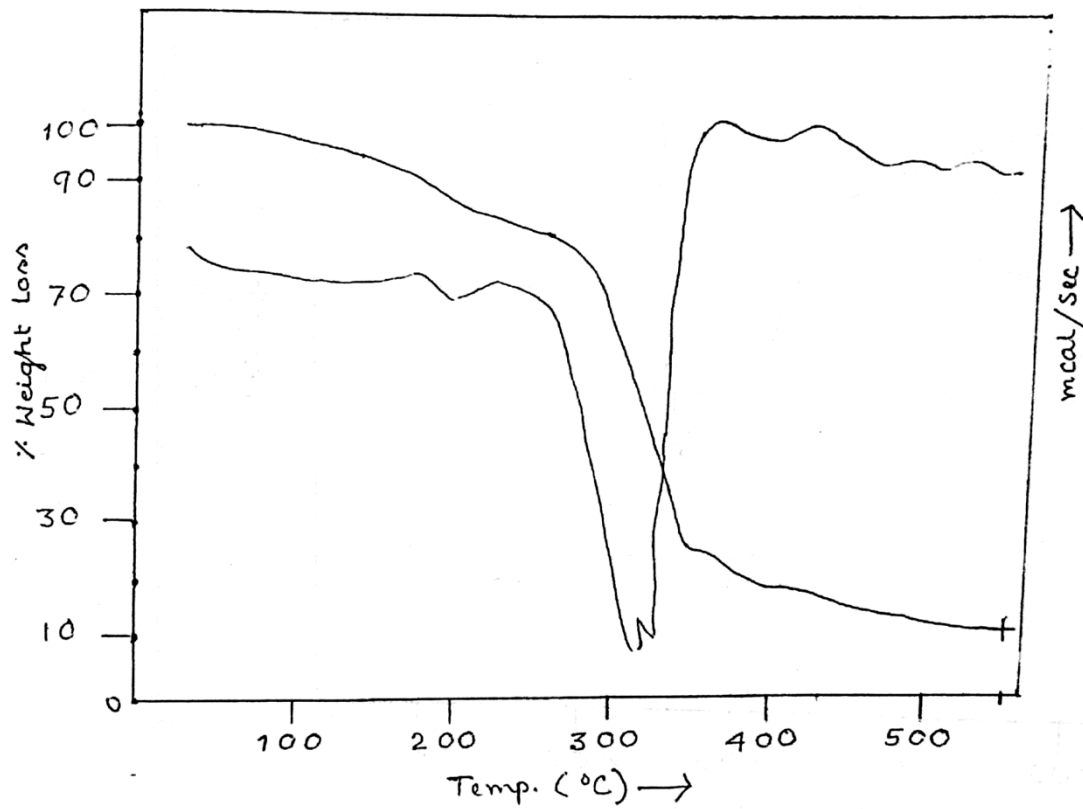

Figure 4. XRD of PU$_{2.25}$

Figure 5. Thermogravimetric Analysis and DSC Analysis of $PU_{2.0}$
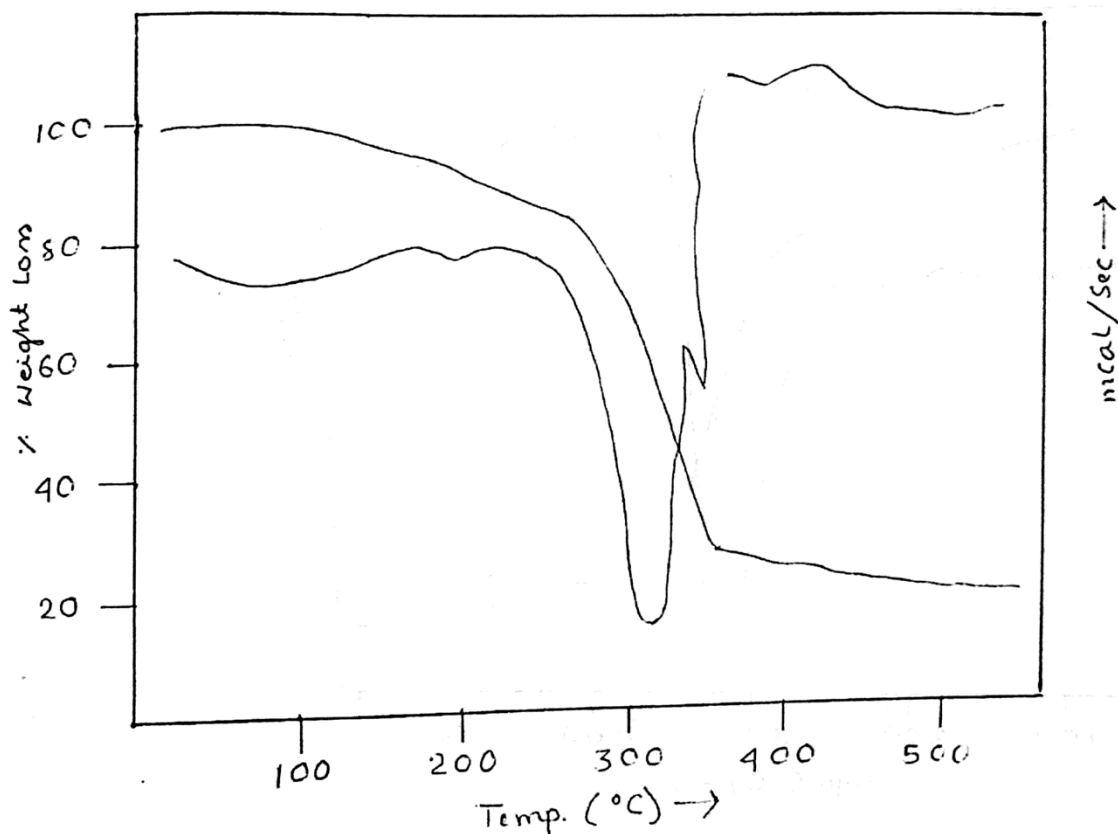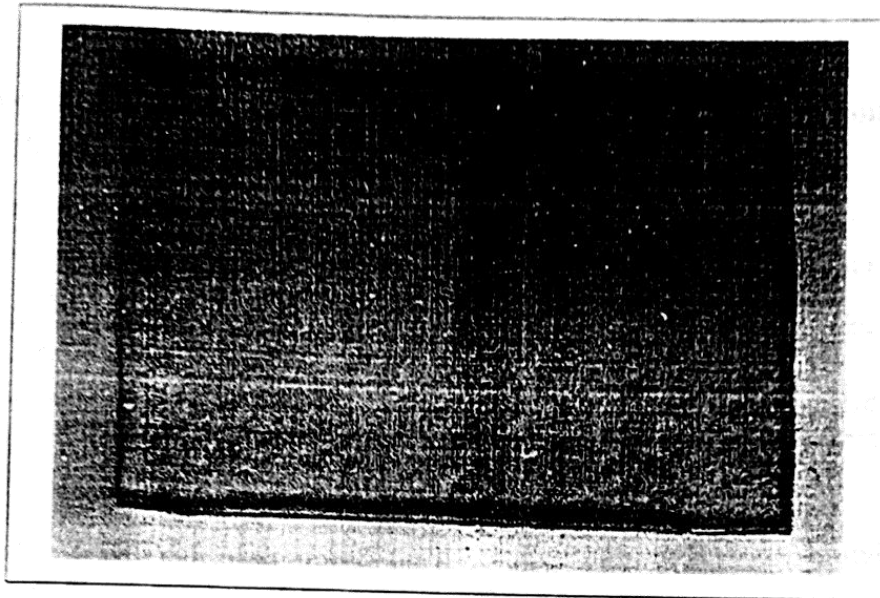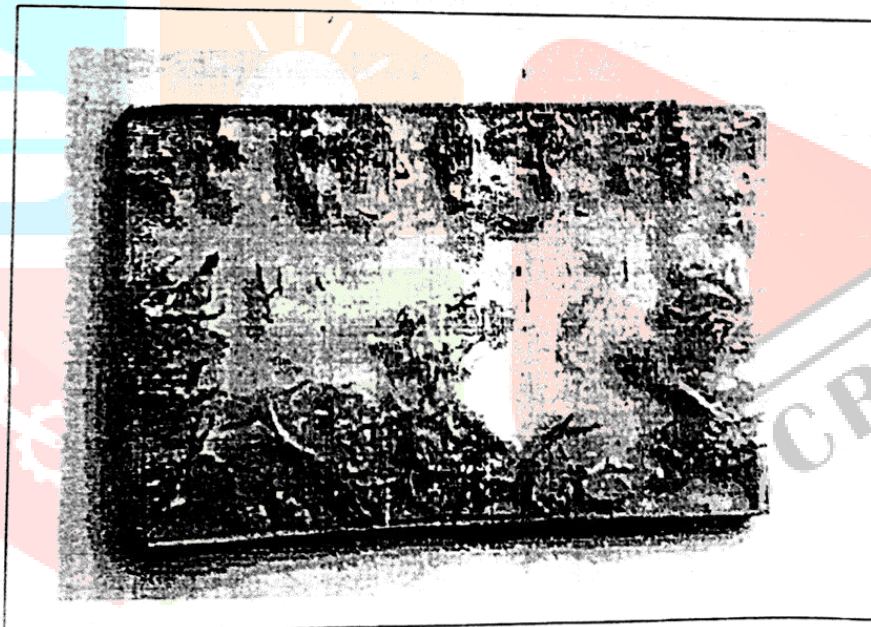
Figure 6. Thermogravimetric Analysis and DSC Analysis of $PU_{2.25}$

Photograph of the sample before soil burial test

Photograph of the sample after soil burial test

Figure 7

Table 1. Composition and physical properties of synthesized polyurethane

Sample code	NCO/OH ratio (mole)	Density (gm/cc)	Appearance
$PU_{2.0}$	2:1	1.08	Light yellow
$PU_{2.25}$	2.25:1	1.17	Light yellow

Table 2. IR Peak Assignments for Ester diol

Wave number (cm^{-1})	Peak assignment
3400	OH group
2889	Aliphatic C-H stretching
1735	C=O group
1357'1460	Aliphatic C-H deformation
1249'1122	C-O anti symmetric and symmetric stretching

Table 3. IR Peak Assignment for Polyurethane film (PU $_{2.25}$)

Wave number (cm^{-1})	Peak assignment
3483	N-H stretching
2869	C-H stretching
2275	Free NCO group
1689	Urethane linkage

Table 4. Mechanical Properties of the Synthesized Polyurethane

Sample	NCO/oh ratio (mole)	Tensile strength (Mpa)	Specific tensile strength (Mpa)	Elongation at break (%)
PU $_{2.0}$	**2:1**	**3.87**	**3.58**	**61.02**
PU $_{2.25}$	**2.25:1**	**4.31**	**3.68**	**59.71**

Table 5. Thermal Degradation and Weight Loss Characteristics of Polyurethanes by Thermogravimetric Analysis

Sample Code	NCO/OH ratio (mole)	Temperature range (°C)	% Wt.loss
PU $_{2.0}$	**2:1**	**157↔234**	**7**
		234↔369	**60**
		369↔434	**6.5**
		434↔550	**3**
PU $_{2.25}$	**2.25:1**	**177↔227**	**5**
		227↔369	**49**
		369↔419	**2**
		419↔527	**3**

Table 6. Hydrolytic Stability of Polyurethane (PU $_{2.0}$) in Mineral Acids

Exposure time (Day)	% wt. Loss in 10% HCL	% Wt. Loss in 10% H$_2$SO$_4$	% Wt. loss in 10% HNO$_3$
1	6.7	6.12	7.33
4	8.05	7.48	9.26
10	8.71	8.46	11.64
17	13.5	11.14	15.15

Table 7. Stability of Polyurethane (PU$_2$.) in Aqueous Alkali Solution (10 %NAOH)

Immersion time (Day)	% Wt.loss
1	13.65
4	21.97
7	50.87

Table 8. Stability of polyurethane (PU$_{2.0}$) in Saline Water (10% NaCl)

Immersion time(Day)	% wt. gain
4	2.5
7	3.61
10	3.8

Table 9. Stability in Water

Immersion time (Day)	% Wt. loss
4	8.35
10	9.60
17	13.26

Table 10. Solvent Resistance

Solvent	% Wt. gain after 5 hours	% Wt. gain after 7 hours
Chloroform	1.17	2.7
Toluene	1.05	1.9
Tetrahydrofuran(% Wt. loss)	15.7	21.2

Table 11. Soil Burial Test

Time (Day)	% Wt. loss
24	8.94

5.1 Summary

1. Lactic acid (LA) was esterified with PEG-200 to form an esterdiol.

2. The esterdiol thus produced was reacted with TDI to produce polyurethane in presence of DBTDL acting as catalyst.

3. The polyurethane produced in this case was amorphous in nature.

4. The polyurethane produced shows good mechanical strength.

5. On increasing the NCO/OH molar ratio the tensile strength increases.

6. The synthesized polyurethane shows good thermal stability at the working temperature. So, there is no chance for thermal degradation during use.

7. The polyurethane has moderate stability in dilute acids and poor stability in dilute alkali.

8. The polyurethane has good stability in saline water.

9. The polymer is stable in different solvents but swells slightly in polar solvents.

10. The polymer degradates slowly when burred in soil.

Scope of the Present Investigation

Many polymers have been synthesized for application as biodegradable materials particularly in biomedical applications. Out of those polymers mostly polyesters and polyester based polyurethanes have found wide application as biodegradable materials. Few of them are commercially available for use as biodegradable sutures, controlled drug delivery system etc. These polymers are not supposed to release fragments toxic to the living systems, i.e., the degraded polymers should be excreted or absorbed in the body without imparting any harmful effect. While these polymers have found suitability in terms of biocompatibility and nontoxicity, but they are expensive. So there lies a scope for the development of cheaper nontoxic, biocompatible and strong biodegradable polymers using cheaply available staring materials.

Conclusion

The aim of the project was to develop a biodegradable polyurethane, which will have biomedical applications. This prepolyurethane in this present investigation is one component system and can be cured at room temperature by exposing to moisture.

This polymer possesses good mechanical strength, thermal stability and solvent resistance. Upon exposure to soil it shows good amount of degradation. It is amorphous in nature and thus fulfils the criterion of being used in biomedical application.

The cost of production of this polymer is also very low as inexpensive starting materials are used.

If further developments are done in this system then a novel biomaterials might be obtained which will have wide use in biomedical applications.

Declaration of interest statement: This work is not in conflict with any other work by any researcher anywhere.

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