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# Synthesis and molecular characterization of chitosan based polyurethane elastomers using aromatic diisocyanate

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ABSTRACT

The present research work was performed to synthesize a new series of chitosan based polyurethane elastomers (PUEs) using poly(ε-caprolactone) (PCL). The chitosan based PUEs were prepared by step-growth polymerization technique using poly(ε-caprolactone) (PCL) and 2,4-toluene diisocyanate (TDI). In the second step the PU prepolymer was extended with different mole ratios of chitosan and 1,4-butane diol (BDO). Molecular engineering was carried out during the synthesis. The conventional spectroscopic characterization of the synthesized samples using FT-IR confirms the existence of the proposed chitosan based PUEs structure. Internal morphology of the prepared PUEs was studied using SEM analysis. The SEM images confirmed the incorporation of chitosan molecules into the PU backbone.



## 1. Introduction

Now a day's polyurethanes (PUs) are one of the most famous and adaptable materials of the world. They are an important division of synthetic polymers that have been extensively used in biomedical applications and various industries especially motor vehicles. A lot of products e.g., furniture coatings, synthetic resin, construction materials, fibers, paints, elastomers, synthetic leathers and synthetic skins contain polyurethane [1,2]. The urethane linkages is the repeating unit in PUs produced from the reaction of an isocyanate (—NCO) with an alcohol (—OH). The main repeating units in PUs are urethane groups while the other units like urea, ester, ether and aromatic may also be present in the structure [3]. Polyurethane elastomers are probably the most malleable group of polymers because they can be molded, injected, extruded and recycled [4]. Synthetic polyurethane elastomers are widely utilized as engineering materials in various industries and are well known for their outstanding properties [5]. From a generic point of view it is accepted that better properties are achieved as the micro-phase segregation is increased between the soft and hard blocks. The existence of the phase segregation caused by the clustering of hard and soft segments into separate domains has been a subject of continued research interest [6]. It is important to consider that efficient packing in hard domains is largely driven by the amenability to strong hydrogen bonding between the hard segments of adjacent chains. Various polyols, diisocyanates and chain extenders have been used in the synthesis of PUs and their effect on the properties have been investigated [6,7]. The constitution of the chain extender has a major effect on properties and morphology of polyurethanes. A number of literature have also mentioned that properties of chain extender (CE) such as the chemical structure, chain length, molecular volume, functionality and biochemical nature can manipulate hard segment packing which support the crystallization in the hard domains [8,9].

In the biomedical fields, the PUEs replace all other synthetic and natural polymers such as natural rubber, poly(ethylene), poly(vinyl chloride), fluoropolymers and silicones [10,11] because of the interesting mechanical properties, imitate the behavior of different tissues, relatively good biocompatibility [12] and easily become the part of human body because they contain urethane linkage which is analogous to the peptide linkage that present in proteins. So, they are used in making absorbable and non-absorbable sutures, heart valves, aortic grafts, dialysis membranes, insulation pacemaker electrodes, catheters, intra-aortic balloons and breast

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implants [13]. Many modifications have taken place in the PU structure for the preparation of biodegradable PUEs through the incorporation of suitable chain extender in the backbone of PU such as chitin [14] and starch [15,16] to enhance anti-thrombogenicity and biocompatibility.

Polysaccharides such as cellulose, starch, chitin, chitosan, dextran, pectin, alginic acid, agar, agarose, starch, carrageenan, and heparin etc. can be obtained from different natural sources. These natural polysaccharides have widely different molecular structure and properties. These natural polymers possess specific structure as well as characteristics which differentiate from those of other synthetic polymers which have vital role in various field of life [17]. Amongst the numerous types of polysaccharides, three types of polysaccharides such as cellulose, chitin and chitosan are the imperative sources of biomass. Production factory of cellulose is plants whereas chitins, poly(β-(1→4)-N-acetyl-D-glucosamine) are synthesized by mainly lower animals such as crustaceans. Chitosan is the amino polysaccharide copolymer of 1,4-D-glucosamine and N-acetyl glucosamine and the most important derivative of chitin. After the extraction of chitin, one can easily derive chitosan by alkaline or enzymatic de-acetylation of chitin [18]. Chitin and chitosan possess similar polymeric backbone while the latter is a de-acetylated product. It has been reported in the literature that when the degrees of de-acetylation (DD) increases from 60%, the chitin transform into chitosan [19].

Chitosan, chitin and cellulose are structurally similar, cellulose contain hydroxyl (—OH) group at C-2 position and chitin contain acetamide groups ($—NHCOCH_3$) while chitosan contain amino group ($—NH_2$) at that position. Chitosan differ from other most commercial polysaccharides in the sense that it occurs in basic form whereas latter are seen in neutral or acidic form [20]. Chitosan chains are able to interact with anion molecules by electrostatic interactions, so the nanoparticles may be formed from chitosan by ionic gelation with polyphosphates [21] and with nucleic acids [22]. However, solubility of chitosan is lower extent in water at pH neutral or basic because under these conditions chitosan surround the free amino groups. The neutral $—NH_2$ group is not enough polar to neutralize the polymeric chain in the presence of inter-chain hydrogen bonding of —OH group. Chitosan is soluble in water in acidic media because in this media protonation of amine functions take place. So, the solubility is subjected to division of free amino groups and N-acetyl groups [23,24]. In such cases, the existence of positive charges on the chitosan skeleton enhances the solubility due to the repulsion between the different polymer chains. In organic solvents such as dimethyl sulfoxide (DMSO) and p-toluene sulfonic acid chitosan are poorly soluble [25]. This low solubility is a limitation for the treatment of chitosan and also a barrier to chemical modification. To overcome this disadvantage, the chitosan oligomers are sometimes preferred. These oligomers (polymerization degree 20) are much more water soluble than their polymeric counterparts, even at a functional pH. Several methods for the synthesis of oligomers of chitosan have been reported, mainly based on acid hydrolysis at high temperature. However, in this study chitosan was dissolved in DMSO following the lower molecular fragments of chitosan with dilute hydrogen peroxide.

As discussed above, PU shows inherent biocompatible behavior which can be enhanced by incorporation of polysaccharides such as chitosan, chitin and starch moieties. If these polysaccharides are introduced as chain extender in the backbone of PU as a part of hard segment also favors to produce new biomaterials with excellent biocompatibility. In chitosan there are two —OH groups located at C3—OH and C6—OH position of chitosan and one amide ($—NH_2$) group at C2-position. The hydroxyl and amide functionalities of this biopolymer allow chemical reactions with PU prepolymer. Due to the absence of any comprehensive report on the molecular engineering of chitosan based PUEs this project is designed to synthesize novel chitosan based PU via a standard two-step reaction procedure; using polycaprolactone (PCL) diol (CAPA 2200A, molecular weight 2000) as macrodiol, toluene diisocyanate (TDI), 1,4-butane diol (BDO) and chitosan (CS).

**Table 1**
Sample code designation and different formation of chitosan based PUEs.

| S. No | Sample code | TDI[a] (mole) | PCL[b] (mole) | Cs[c] (mole) | BDO[d] (mole) |
|---|---|---|---|---|---|
| 1 | SPU1 | 3 | 1 | 0.0 | 2.0 |
| 2 | SPU2 | 3 | 1 | 0.5 | 1.5 |
| 3 | SPU3 | 3 | 1 | 1.0 | 1.0 |
| 4 | SPU4 | 3 | 1 | 1.5 | 0.5 |
| 5 | SPU5 | 3 | 1 | 2.0 | 0.0 |

[a] 2,4-Toluene diisocyanate.
[b] Polycaprolactone macrodiol.
[c] Chitosan.
[d] 1,4-Butandiol.

## 2. Experimentals

### 2.1. Chemicals

Aromatic diisocyanate i.e., 2,4-toluene diisocyanate (TDI) and chain extender/crosslinker i.e., chitosan (with 80% degree of de-acetylation) and 1,4-butane diol (BDO) were purchased from Sigma–Aldrich Chemical Co. Macrodiol i.e., polycaprolactone macrodiol, CAPA 2200A (molecular weight 2000) were obtained from Solvay Chemicals Co. Polycaprolactone macrodiol (CAPA) and chain extender such as BDO used in this study were dried at 80 °C under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. Molecular weight of CAPA 2200A was confirmed by applying the procedure reported in ASTM D-4274C [26]. All other materials including TDI and chitosan were used as-received. All the reagents used in this work were of analytical grade.

### 2.2. Synthesis of PU based on BDO (SPU1)

For this investigation isocyanate (NCO) terminated polyurethane (PU) prepolymer was synthesized according to a recommended procedure [14]. Following the procedures, the diisocyanate like 2,4-toluene diisocyanate (TDI) was reacted with macrodiol e.g., polycaprolactone (PCL) with mole ratio (3:1) to obtain isocyanate (—NCO) terminated PU prepolymer. For this purpose 1 mole of macrodiol (i.e., PCL) was placed into a four necked reaction kettle equipped with reflux condenser, mechanical stirrer, heating oil bath, dropping funnel, $N_2$ inlet and outlet. The temperature of the oil bath was increased to 60 °C. Then 3.0 moles of diisocyanate (i.e., TDI) was added and the temperature was then increased to 100 °C. During optimization of experimental condition it has been confirmed that NCO terminated PU prepolymer formed in 1 h. The NCO contents in the PU prepolymer were determined by titration with n-butylamine [26]. The PU prepolymer was transformed into the final PU in chain extension step. In this step the PU prepolymer was persuasively stirred by mechanical stirrer at 80 °C and then previously degassed chain extender (i.e., 1, 4-butane diol, 2 mole) was added following the formulation given in Table 1. When homogenous mixture was gained in the flask, the dispersion of the chain extender was considered complete and then the viscous polymer was poured into a Teflon plate to form a uniform sheet. The prepared PU sample were placed in vacuum for 10–15 min to make sure the elimination of air bubbles prior to casting and then cured for 24 h in hot air circulating oven at 100 °C. Schematic illustration of chemical route for synthesis of polyurethane based on BDO (SPU1) is shown in Fig. 1(a).