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Curcumin incorporated polyurethane urea elastomers with tunable thermo-mechanical properties

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ABSTRACT

Polyurethane urea (PUU) elastomers were synthesized using 1,4-diaminobutane (DAB) as a chain extender, hexamethylene diisocynate (HMDI) as a hard segment and polycaprolactone (PCL) as a soft segment with different concentrations of curcumin (CUR). A series of curcumin polyurethane ureas (CURPUU) containing different mole ratio of: CUR: PCL (0:100, 15:85, 25:75 and 35:65) were synthesized and characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile strength, scanning electron microscope (SEM) and contact angle to study the effect of curcumin on the polymer properties. Thermal analysis revealed that CURPUU with the mole ratio 15:85 of CUR: PCL exhibited better thermal stability. The observed tensile strength, breaking strain and initial modulus were found to be in the range of 7.34 to 19.08 MPa, 213.20 to 925.38% and 2.18 to 23.33 MPa respectively. The hydrophobicity of CURPUU film increased by increasing the ratio of curcumin. The morphological characterizations of PUU were revealed by SEM. UV-Spectrophotometer was employed to investigate the physically entrapped curcumin into CURPUU elastomers. Finally, antimicrobial activity of all the PUU samples was investigated against two bacterial strains (*E. coli* and *S. aureus*) which exhibited that these elastomers can be used as potential biomedical materials.

1. Introduction

Polyurethanes (PU) find their applications in biomedical devices such as tissue regeneration scaffolds [1], drug delivery systems [2] and resorbable implants [3]. The PU has been widely used in different fields with ever growing demands day by day. The properties of PU can be modulated by fine tuning of its structure by making composites materials, blends, hybrids and copolymers. Different methodologies can also be used for the synthesis of PU with fascinating properties [4,5]. Structural diversity of diisocynates, diols and chain extenders offer numerous possibilities for designing PU with required microphase morphologies and thermo-mechanical properties [6–10]. The availability of variety of chain extenders, both diol and diamine provide many possibilities to tune the characteristic properties of PU. Application of diamine based chain extender imparts urea linkage, alternating with urethane linkage in the polymer backbone which provides symmetric bidentate hydrogen bonding that results in increase in tensile strength, modulus and parallely decrease in elongation [11–13].

There are several key requirements in designing biodegradable PU: incorporation of biocompatible components, bioactivity, tissue like mechanical properties and suitable degradation rate. Incorporation of bio-based moieties in the traditional structure of PU satisfies the unique design requirements of biodegradable PU [13]. Several bio-mimic synthetic materials have been developed by incorporation of PU with natural materials i.e. alginates [14], cellulose [15], starch [16], chitin [17], glucomannan [18], heparin [19], dextrin [20], chitosan [21] and curcumin [22] etc.

Curcumin is a natural bioactive compound that possesses antioxidant, antibacterial, anti-proliferative, anti-inflammatory, anti-amyloidogenic and anti-carcinogenic properties [23]. Because of these therapeutic properties of curcumin, numerous studies have been devoted to incorporate curcumin with polymeric materials to design biodegradable, biocompatible and bioactive materials. Curcumin has been successfully incorporated into polymeric hydrogels to synthesize potential biomaterials such as curcumin containing PU hydrogels with mechanical tunability for applications in scaffolds and implants in tissue engineering [24] and antioxidant β-amino esters hydrogels to reduce oxidative stress on cells [25]. Curcumin containing PU

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elastomers have also been synthesized to enhance antiplatelet behavior [26]. Hence, curcumin can be incorporated successfully in PU. Recently, a different approach has been implemented to blend chitosan with curcumin in order to improve antimicrobial and biocompatible properties of PU. [27]. Although antimicrobial properties were enhanced by incorporation of chitosan/curcumin with PU but mechanical properties were not so much impressive to be used for biomedical applications. Herein, we reported the synthesis and characterization of novel curcumin based PUU elastomers. According to best of our knowledge, we are reporting first time the addition of varying amounts of curcumin in the initial step of polymerization (prepolymer synthesis step) along with the Polycaprolactone (PCL) (soft segment), 1,6-hexamethyldiisocynate (HMDI) (hard segment) and 1,4-diaminobutane (DAB) as a chain extender. Structural and thermo-mechanical characterization is performed to evaluate the effect of curcumin on tensile strength, thermal and antimicrobial properties of resulting polymers. The noteworthy thermal stability and mechanical strength are observed in our curcumin PUU and there is no need for further incorporation of bio-functional moieties.

2. Material and methods

2.1. Chemicals

Polycaprolactone diol (number average MW = 2000, PCL-diol, Acros Organic) was dried under vacuum at 50 °C for 1 day to remove the moisture. Curcumin (Admas China), 1,4-diaminobutane (DAB, Sigma Aldrich), 1,6-hexamethyldiisocynate (HMDI), dibutyltin dilaurate (DBTDL), dimethyl sulfoxide extra dry (DMSO, ultrapure ≥ 99.9%, Acros Organic) and 1,1,1,3,3,3-hexafluoroisopropanole (HFIP) used as received.

2.2. Synthesis of curcumin polyurethane urea

Curcumin based PUU was synthesized from PCL, curcumin, HMDI and DAB as a chain extender by following previously reported two-step solvent polymerization method [28,29] as shown in the Scheme 1. The (CUR + PCL): HMDI: DAB molar ratio was defined as 1:2:1 (Table 1). In first step, curcumin and PCL were mixed at different mole ratios: 0/100, 15/85, 25/75 and 35/65, and dissolved in DMSO in a four-neck flask under inert environment of highly pure nitrogen at 70 °C with vigorous stirring until the mixture was homogenized. After that, HMDI was added into four-neck flask with the few drops of DBTDL as catalyst. The reaction was carried out for 4 h at 70 °C and after 4 h the solution was cooled to room temperature and chain extender solution (DAB/DMSO) was added dropwise with the help of dropping funnel. Then the final polymer solution was kept in oil bath at 70 °C for 20 h with constant stirring. The synthesized CURPUU were precipitated in an excess amount of cool deionized water to remove the solvent and unreacted curcumin, and then dried in vacuum at 60 °C for 3 days. The synthesized CURPUU with different mole ratio of curcumin: PCL as mentioned above are named as CUR_0PUU, CUR_{15}PUU, CUR_{25}PUU and CUR_{35}PUU, respectively.

2.3. Film casting

The synthesized CURPUU were completely dissolved in HFIP to prepare 10% solution and poured onto a Teflon plate. All the CURPUU were cured at room temperature, and vacuum oven was used at 60 °C for 3 days to dry the film in order to completely remove the residual solvent. The obtained film thickness was about 1 ± 0.1 mm.

3. Characterizations

3.1. Spectroscopic analysis

ATR-FTIR spectrometer (Bruker Alpha) was used for the structural characterization of PUU films, range from 4000 to 500 cm^{-1}. The spectra were taken as the average of 24 scans at a resolution of 4 cm^{-1}.

UV–Vis spectrophotometer (Shimadazu 2500) in the range of 200–800 nm was used to investigate the physically entrapped curcumin in PUU elastomers.

3.2. Tensile properties

Mechanical properties of CURPUU were determined according to ASTM D 638 with the cross-head speed of 5 mm/min by using the Electronic universal material testing machine (Model CMT4204). Cycling tensile properties were also analyzed under the same conditions. CURPUU samples marked at their distal ends, elongate to 10% and kept at this position for 1 min and then released. The same process was repeated 3 times and then change in length was observed after the release of load. Instant strain recovery was calculated as $(1 - (L_1 - L_0)/L_0) \times 100\%$.

L_0 = original length
L_1 = after releasing the load.

3.3. Thermal analysis

3.3.1. DSC analysis

The glass transition temperature (Tg) and melting temperature (Tm) were determined by differential scanning calorimetry (DSC) by TA (Q20) instrument with scanning rate of 10 °C/min from −75 to 250 °C and 10 mg of sample was used.

3.3.2. Thermogravimetric analysis

Thermal degradation of CURPUU were characterized by using thermogravimetric (TGA Q50) instrument under the temperature range from 100 °C to 600 °C with the heating rate of 10 °C/min under nitrogen and 10 mg of sample was used.

3.4. Antimicrobial activity

Agar diffusion method was used to determine the antimicrobial activity of the CURPUU films. The CURPUU films were cut into 6 mm diameter in circular shape (discs) and washed with ethanol. Polymer discs placed on the agar plate petri dishes containing bacterial strains (*E. coli* and *S. aureus*) were incubated at 37 °C for 12 h, after that inhibition areas were measured.

3.5. Surface characterization

3.5.1. Scanning electron microscopy (SEM)

Surface morphology is an important characteristic for the polymers in field of biomedical applications. Synthesized CURPUU were characterized by SEM (S-4800, Hitachi Co., Japan) and scanned at an accelerated voltage of 20 kV.

3.5.2. Contact angle

The static contact angle was measured by sessile drop method with a (JC2000 (Voltage 220 V, frequency 50 Hz)). In this method, a drop of water was placed on a surface of CURPUU film and pictures of the water drop were taken by high resolution camera and calculated the contact angle by software. The contact angle was taken as an average of 3 repetitions.