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ONE-POT AND SOLVENT-FREE SYNTHESIS OF CARBODIIMIDE MODIFIED CHITOSAN; EXTRAORDINARY THERMAL STABILITY

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Abstract. A facile, one-pot, and solvent-free synthesis is demonstrated to obtain a thermally stable chitosan biopolymer. In this work, a bifunctional isocyanate molecule is reacted with chitosan to form urea and urethane bonds between chitosan chains. Subsequently, the designed chemistry facilitated the formation of carbodiimide bonds between chitosan chains via dehydration of the urea bond. The modified chitosan is superior in thermal properties with $T_{10\%}$> 400°C and char yield of 65%. The modified chitosan can be used as a thermally stable bio-filler. This synthetic methodology is a facile route to achieve improved thermal stability in biopolymers.

Keywords: chitosan, one-pot synthesis, carbodiimide, porous morphology, thermal stability.

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Introduction

Improving the thermal stability of biopolymers is one of the emerging areas as it can extend the application of renewable polymers into several key technological areas, such as aerospace and military. Chitosan is a well-known biopolymer, extensively used in the biomedical field for tissue engineering, drug delivery, and for many applications [1-4]. Because of the poor thermal stability, chitosan is rarely explored for thermal applications. Generally, chitosan molecules start to degrade between 200-220°C (main chain), and the moisture absorption is high due to the presence of polar amino and hydroxyl groups [5-7]. Two popular approaches employed for enhancing the thermal properties of chitosan are i) chemical modification by utilizing amino and hydroxyl groups of chitosan and ii) addition of inorganic fillers into chitosan.

Previously, lactic or glycolic acid chains were covalently bonded to chitosan and was found that thermal stability was not improved [8]. A modification of chitosan with Schiff's base structure did not yield significant improvements in thermal stability [9]. Modification of chitosan with benzophenone reduced its thermal performance compared to that of chitosan alone [10]. However, aldehyde-modified chitosan improved the char yield when incorporated into the thermoplastic polyurethane matrix [11]. An alternative technique is to add inorganic fillers to enhance the thermal properties of chitosan. There were attempts to increase both thermal and biological properties with inorganic nanoparticles. To improve the thermal stability, chitosan silica hybrids were studied [12]. The sol-gel route improved the stability beyond 250°C. In this method, the maximum char yield observed was 47%. In another study, ZnO nanoparticles were introduced into chitosan but failed to reach the degradation temperature >250°C [13]. However, on attaching carbon nanotubes to chitosan, the $T_{10\ \%}$ achieved was between 350-375°C [14]. Organosilica-chitosan cross-linked nanospheres also could not show a significant change in thermal stability [15]. Low thermal properties have been observed for graphene and montmorillonite clay-modified chitosan [16,17]. When MgO nanoparticles were added, an increase of 27-37% in thermal stability was achieved [18]. The $CaCO_3$ particles were also used to prepare chitosan nanocomposites but resulted in moderate improvement [19].

Chitosan-aromatic aldehyde Schiff base derived by the condensation reaction of chitosan indicated different thermal stability than pristine polymer [20]. Investigation on the thermal stability of antioxidant films based on chitosan (CH) and Maillard reaction products (MRPs) derived from cod skin collagen peptides pointed out that incorporation of MRPs (0–10%) had little effect on the thermal stability of chitosan films [21]. Another study was carried out to investigate the change in thermal behavior of chitosan films after the addition of sorbitol content in different proportions and found that the decomposition temperature of chitosan was nearly invariable with the change of the content of sorbitol (thermal stability of chitosan films was not reduced, either) [22]. The reinforcement of *chitosan-cellulose nano whiskers composites film* with multiwall carbon nanotubes (MWCNTs) experienced a significant improvement in mechanical properties and also increased the thermal stability by delaying the degradation of CS/CNWs [23]. It has been proved that thermal stability of chitosan obtained from the shells of swimming crab through the subcritical water pretreatment is higher than that of chitosan prepared *via* sodium hydroxide pretreatment [24]. Systematic investigation confirmed that thermal stability of chemically modified chitosan using itaconic acid (a natural unsaturated dicarboxylic acid) is higher than that of the original chitosan film, and the modified chitosan exhibited flame-retardant properties [25].

In this work, an attempt is made to modify chitosan with a significant increase in thermal stability *via* an easy solvent-free synthetic route.

Experimental

Materials

Chitosan powder (Otto, India, deacetylation >80%) was dried at 110°C for 3 hours before use. Toluene diisocyanate (97%, 80:20 isomer mixture, Alfa Aesar, UK) was used without further purification. Distilled water was used from an in-house facility.

Instruments

The *FTIR characterization* was conducted on a Perkin Elmer Spectrum GXA FTIR spectrometer in the wave number range of 4000–400 cm^{-1}. The *elemental composition* (carbon, nitrogen, and hydrogen) was estimated using a Thermo Finnigan EA 1112 Series Flash Elemental Analyzer. The *thermogravimetric analysis* (TGA) of the samples was performed by using TA instruments 2960 from 30 to 900°C in a nitrogen atmosphere at a heating rate of 10°C/minute.

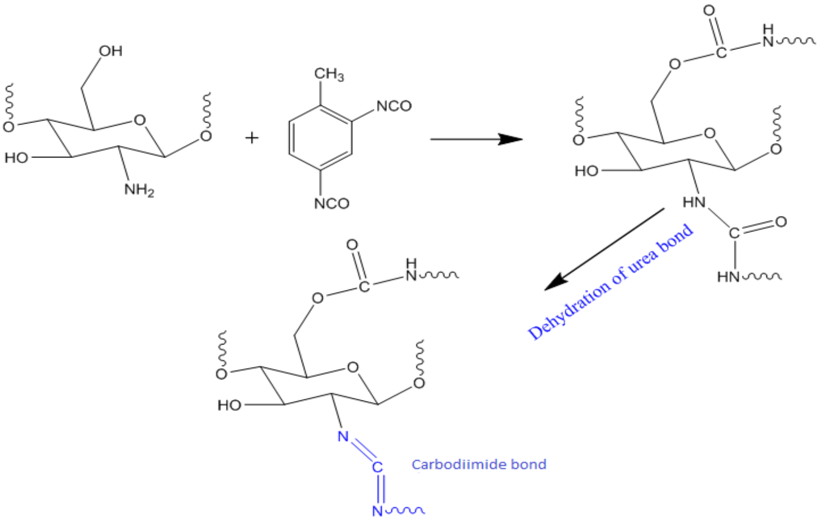
The *morphology* of chitosan and carbodiimide modified chitosan was carried out on a Hitachi SU6600 variable Pressure Field Emission Scanning Electron Microscope (FESEM) instrument. The samples were dried for 24 hours at 110°C to remove the surface moisture, then cut into thin slice and sputter coated (gold) for the analysis into FESEM unit; the images were captured at ambient temperature and vacuum conditions.

Synthesis of carbodiimide modified chitosan

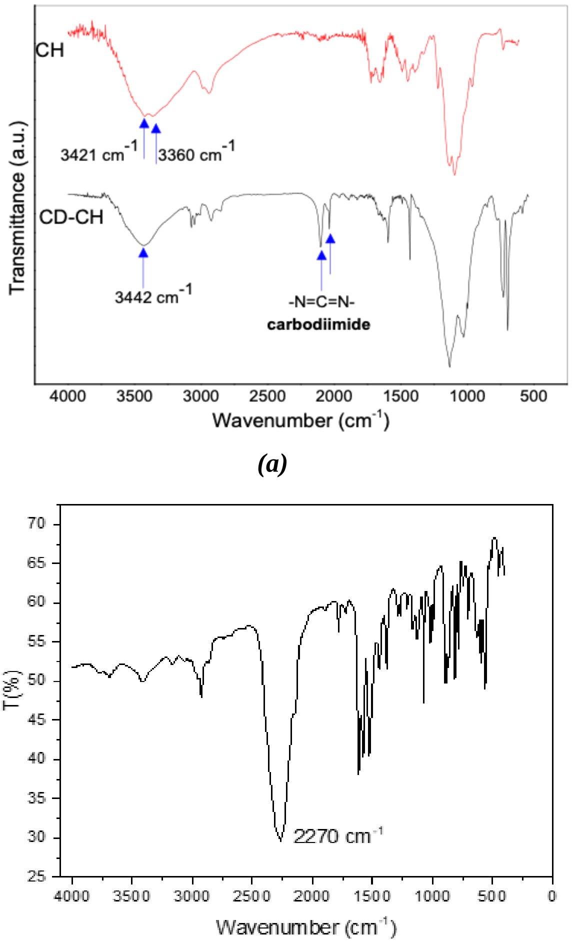
CH powder (0.5 g) and toluene diisocyanate (TDI) (5.0 g) was incorporated in a glass bottle (25 mL), purged with nitrogen gas, and tightly closed. The carbodiimide modification was carried out without the use of any solvent. The reaction mixture was magnetically stirred at 80°C. A viscous slurry was formed after 30 minutes of reaction. The reaction was continued for another 2 hours. Subsequently, the hot viscous mixture was immediately precipitated into 100 mL of distilled water. The powder was washed in distilled water and dried at 70°C under vacuum to obtain light-yellow colored carbodiimide modified chitosan (CD-CH).

Results and discussion

A one-pot reaction was carried out between chitosan and a diisocyanate molecule which possesses high reactivity to primary amino and hydroxyl groups of chitosan. The reaction pathway, morphology, and thermal stability was investigated. Carbodiimide chitosan was synthesized according to the Scheme 1.



Scheme 1. Chitosan–isocyanate reactions lead to the formation of the urea bond and eventually to carbodiimide bonds.



(a)

(b)

Figure 1. FTIR spectra of CH and CD-CH display the peaks at 2100 and 2060 cm^{-1} indicates the formation of carbodiimide structure *(a)* and the strong peak at 2270 cm^{-1} is due to the –NCO group in TDI *(b)*.

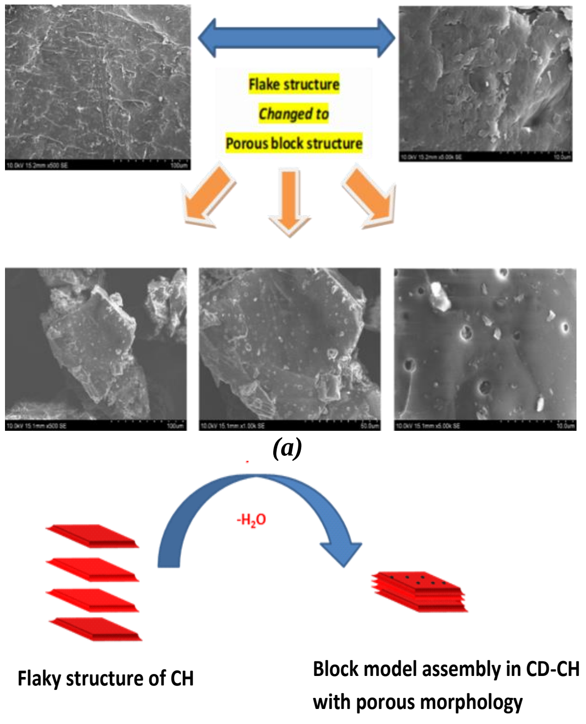
In this procedure, an excess quantity of toluene diisocyanate was used. The liquid isocyanate functioned as a reactant, solvent for chitosan, and dehydrating agent. At the beginning of the reaction – the –NH_2 group of chitosan (as well as OH, but –NH_2 is more reactive) interacted with –NCO of TDI to give urea (-NHCONH-) bonds between chitosan chains. Since TDI is a bifunctional molecule, urea bonds were formed between chains.

The evolution of the urea/urethane bond during the reaction was confirmed by recording FTIR of aliquot where vibrational peaks of –CO- group were observed at 1720 cm^{-1} (urea/urethane carbonyl) along with a peak corresponding to –NCO- at 2270 cm^{-1}. In the progressive FTIR analysis, -CO groups started to disappear and the final product displayed mainly two peaks located at 2100 and 2060 cm^{-1} respectively (Figure 1).

These two are signature peaks of the carbodiimide structure (N=C=N) [26]. Additionally, the amino group in chitosan, observed at 3360 cm^{-1} was vanished/reduced in the FTIR spectrum of carbodiimide-linked chitosan. In addition, peaks corresponding to –CO groups were also drastically diminished. After the formation of the urea bond, excess TDI will act as a dehydrating agent such that it will grab water molecules from the urea bond itself to form carbodiimide links. The reaction between CH and TDI is shown in Scheme 1.

Since the CD-CH was insoluble in many of the solvents, solution-phase NMR studies could not be carried out. The CD-CH particles were insoluble even in 2% acetic acid whereas chitosan was soluble. To acquire more evidence for modification, the nitrogen content of CH and CD-CH was assessed. Surprisingly, the nitrogen content was lower in CD-CH compared to CH. This is theoretically possible because the carbon content of linking molecule TDI is almost 4 times nitrogen content (16 *versus* 62%). Elemental analysis (%): CH: C (40.6), H (6.0), N (7.5); CD-CH: C (48.0), H (3.9) N (3.4). All these studies indicate the extensive and effective modification of chitosan by this route.

The morphologies of pristine chitosan and CD-CH were evaluated by FESEM analyses and the results are presented in Figure 2.



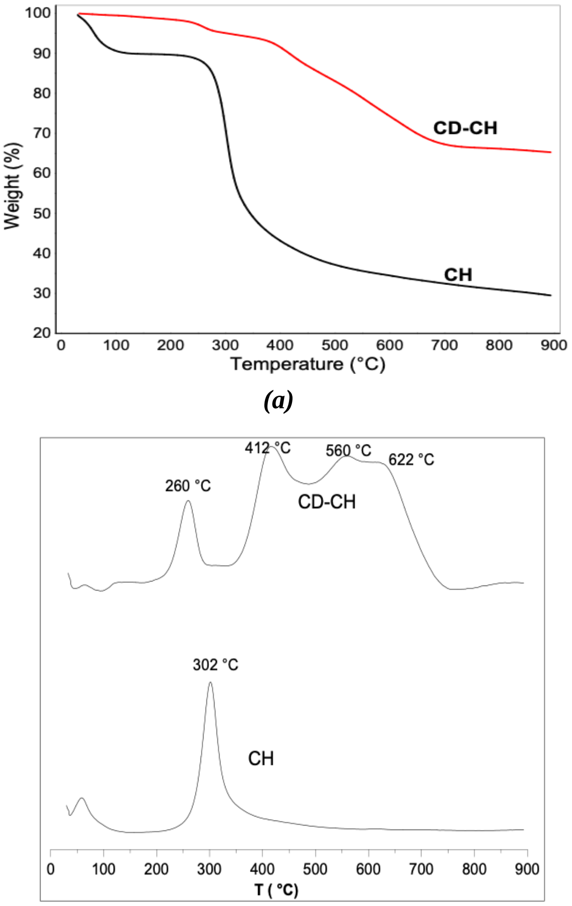
(a)

(b)

Figure 2. FESEM images of CH and CD-CH (500x and 5000x magnifications are shown for both CD and CD-CH. An image of 1000x is also given for CD-CH) *(a)* and formation of coherent block-structured CD-CH *via* carbodiimide bonds *(b)*.

Unmodified chitosan was observed as flakes whereas a coherent and block structure was noted in CD-CH. This implies that chitosan chains were covalently bonded by carbodiimide groups. In addition, pores were observed on the block-structured CD-CH. This pore structure is attributed to the evolution of water molecules during carbodiimide formation (urea-dehydration).

The most striking feature of CD-CH is its thermal stability (Figure 3). The $T_{5\%}$ of CD-CH was 302°C whereas neat chitosan showed below 70°C. The $T_{10\%}$ of chitosan was 125°C but CD-CH exhibited a high value of 413°C. Additionally, the char yield was dramatically improved to 65% at 900°C, from 29% of neat chitosan. The high thermal stability of CD-CH is due to the presence of heteroatoms of high aromatic (phenyl rings) nature. In heterocyclic polymers such as poly(amide-imide)s and polybenzimidazoles, high thermal stability is a typical feature [27,28].



(a)

(b)

Figure 3. Thermogravimetric profiles of CH and CD-CH imply the unusual thermal stability of CD-CH material *(a)* and DTG profiles of CH and CD-CH indicate different degradation pattern due to modification in the polymer chain *(b)*.

The carbodiimide may act as a link between chitosan chains (heteroatoms, especially the stronger -N=C=N- bond uniformly attached among chitosan chains). Also, the CD-CH exhibited < 1 wt.% weight loss up to 150ºC, which is due to the lower moisture absorption capability of CD-CH, compared to chitosan. This implies that polar groups (present in CH) were reduced in CD-CH due to the carbodiimide formation reaction. This is the maximum thermal stability achieved in completely organic chitosan systems. The DTG curves are different for CH and CD-CH. Faster degradation was observed at about 300ºC in CH. In CD-CH, degradation occurs in steps and in a lower rate than CH, this may be the reason for improved thermal stability observed in CD-CH. The higher DTG peaks appeared at 415, 560 and 622ºC indicate the improved thermal stability of CD-CH (but these high temperature peaks were not present in the DTG of CH). The weight loss is less in CD-CH compared to CH.

Conclusions

In this contribution, a simple and single-step method was demonstrated to obtain carbodiimide-modified chitosan. Chitosan was reacted with toluene diisocyanate to yield a urea bond which on dehydration resulted in the carbodiimide links between chains. In this reaction, toluene diisocyanate also has the role of dehydrating agent. The FTIR analysis revealed the formation of the carbodiimide bond with characteristic vibrational peaks noted at 2060 and 2100 cm^{-1}. Due to the loss of water molecules from the polymeric structure, a porous morphology was observed in FESEM images. The most outstanding feature of CD-CH is its thermal stability which registered $T_{10\%} > 400°C$ with a char yield of 65%. This high thermal feature is attributed to the phenyl rings and hetero-structure present in modified chitosan. However, thermal degradation rates were different in CH and CD-CH. A relatively quicker degradation was seen in CH (about 300ºC), whereas in CD-CH, degradation took place in steps. This reduced rate observed in thermal degradation may be the reason for improved thermal stability of CD-CH. The modified chitosan is a thermally stable bio-filler that can offer thermal stability and compatibility to synthetic/biopolymers since it is purely an organic polymer. The synthetic methodology can be adapted to other biopolymers to accomplish thermally stable biopolymers/bio-fillers.

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