

The preparation and thermal properties of chitosan/bentonite composite beads

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Abstract

The biopolymer composites are often used as remarkable adsorbents in treatment of wastewater due to their biodegradable and nontoxic nature. The chitosan/bentonite composite beads, in this study, were obtained by addition of clay into the polymer using solution process. The bentonite was modified with surfactant cetyltrimethyl ammonium bromide (CTAB) before the composite preparation. The morphology of beads was examined by scanning electron microscopy (SEM). Thermal properties of the composite beads were studied by simultaneous thermogravimetry coupled with differential scanning calorimetry (SDT) and differential scanning calorimetry (DSC). TG results showed that the complex decomposition mechanism of the composites depends on the preparation procedure. It was observed that the concentration of NaOH used for composites precipitation affects the final structure of beads. The influence of preparation procedure on the glass transition temperature T_g of chitosan/bentonite samples was not found (T_g values for all samples were about 144 °C).

Keywords: chitosan/bentonite composite beads, thermal decomposition, DSC.

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The water pollution is a result of nearly all aspects of human activities: domestic, industrial and agricultural [1]. One of the biggest producers of wastewater is the dyeing industry. The wastewater is characterized by high organic pollutant content, deep color and significant impact on water quality. Color is wastewater contaminant that can be easily noticed, because even a very small amount of dyes in water is highly visible [2]. Disposing of the colored wastewater has caused a great interest for the human health and sea life [3,4]. Dyes are very inert, therefore it is hard to remove them from wastewaters. Second obstacle for the removal of dyes is the low saturation of wastewater with dye particles. Due to high costs of removal of very small amounts of pollutants from wastewater, the application of conventional processes of dye removal at a large scale is very expensive [3]. Currently, many adsorption methods using chitosan composites are being developed to adsorb dyes as a substitute for conventional wastewater treatment methods [5].

Chitosan is a partially deacetylated polysaccharide, produced from chitin, the world second most important natural polymer [6–8]. The most important resources for production of chitin are two sea arthro-

pods: shrimps and crabs. Chitosan has different characteristics than any other biopolymer, particularly because of the presence of primary amino groups. It is classified as a natural polymer consisting of randomly distributed α -(1,4)-glucosamine and *N*-acetyl-D-glucosamine units (Fig. 1a). Due to the variety of its functional properties it can be used for synthesis of composite materials with other polymers [9]. Amino and hydroxyl groups in the structure of chitosan can serve as the active sites for removal of heavy metals and dyes [10]. If amino groups of chitosan are cationized, they strongly adsorb anionic dyes by electrostatic attraction in the acidic media [11]. However, depending on the pH values, chitosan can either form gel or can be dissolved, because it is very sensitive to pH [12]. Cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon diglycidyl ether and isocyanates have been used to improve chitosan's performance as an adsorbent [13].

One of the many forms of chitosan for the dye removal by adsorption is its gel-bead form. It is used for adsorption in batch or fixed-bed column systems, deposited on an adequate substrate [14–16]. Chitosan is non-toxic, non-corrosive and safe to handle [17,18], which make it feasible in wastewater treatment. The main reasons for the success of chitosan is that it can bind dyes in low concentrations compared to metal salts and is also efficient in cold water. It does not leave residual metals that can cause secondary contam-

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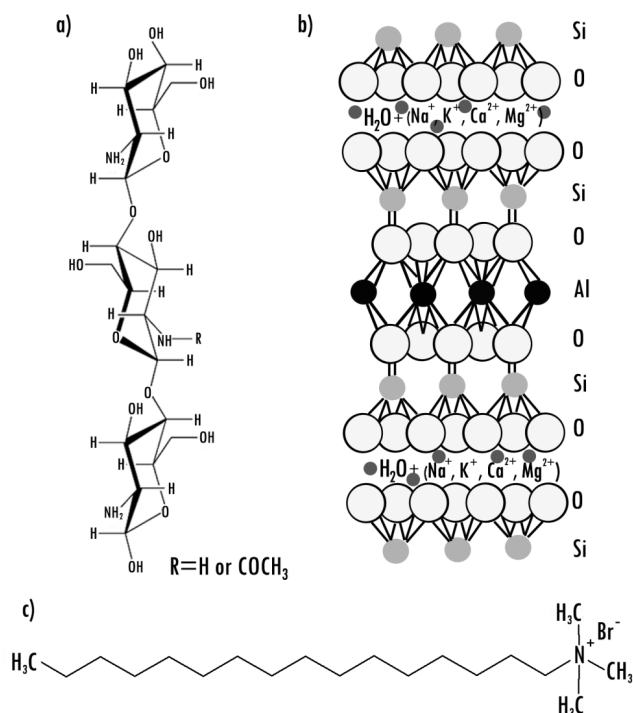


Figure 1. a) Chemical structure of chitosan, b) schematic illustration of layered structure of bentonite and c) chemical structure of CTAB.

ination problems. The low concentrations of chitosan reduce the volume of produced sludge compared for example to alum. Chitosan considerably increases the density of the sludge and facilitates its drying compared to the sludge produced with metal salts. In addition, chitosan is biodegradable, so the sludge can be efficiently degraded by micro-organisms.

Bentonite is a 2:1 type aluminosilicate, its unit layer consists of one Al³⁺ octahedral sheet between two Si⁴⁺ sheets [19]. Because of its large surface area and surface energy, the bentonite exhibits strong adsorption capability. However, negatively charged surface and large amount of exchangeable positive ions make natural bentonite highly hydrophilic and its surface is covered with a layer of water, blocking thus in part its adsorption capability for organic pollutants. By exchanging the occupation of sites on the bentonite surface by organic cations (such as cationic surfactants, quaternary ammonium surfactants), the surface properties can be changed from hydrophilic to hydrophobic. Therefore, bentonite should be modified before use as adsorbent for removal of pollutants from wastewater [1,20–22].

This paper is focused on the synthesis of chitosan/bentonite composite beads for colored wastewater treatment. The influence of the preparation procedure of composite beads on the morphology and thermal behavior of biopolymer composites was studied.

EXPERIMENTAL

Materials

Chitosan (Fig. 1a) of degree of deacetylation >85% was purchased from Aldrich. Bentonite (Fig. 1b) used in this study was obtained from the MTA, Ankara, Turkey. The clay cation exchange capacity (CEC) was 95 meq per 100 g of the clay. This value was estimated directly by exchanging sodium with an ethylenediamine complex of Cu(II) [23]. Cetyltrimethyl ammonium bromide (CTAB) (Fig. 1c), NaOH and acetic acid were of analytical grade and obtained from HIMEDIA.

Sample preparation

Bentonite was firstly dried at 110 °C for 2 h and sieved through 200 μm sieve. The dry bentonite was modified in the following way: 1 g of bentonite was suspended in 100 ml of distilled water at room temperature. CTAB, as a quaternary ammonium surfactant interacts with bentonite by exchanging its sodium ions with quaternary ion. Therefore, CTAB was dissolved in hot water (1 wt. %), slowly poured into the bentonite suspension and stirred for 24 h at ambient temperature. The modified bentonite (mass of 0.5 g) was filtered off, washed three times with deionized water and dried under vacuum. The final product was crushed into powder and sieved again. In order to obtain 2 wt.% of chitosan solution, chitosan was suspended in water at 120 °C for 25 min and then dissolved by addition of acetic acid in a sterile medium. The homogeneous

solution was obtained after stirring for 48 h. Four different chitosan/bentonite composite beads (table 1) were prepared using the following procedure: modified clay was swelled by 50 ml of deionized water, added to 50 ml chitosan solution and stirred at 60 °C overnight. Chitosan shows the polycationic nature in acidic media, and hence, it is suitable for intercalation in bentonite by means of cationic exchange processes, due to the Coulombic interactions between NH_3^+ groups of chitosan and the negative sites in the bentonite structure [24]. The chitosan droplets formed a bead shape in the solution of NaOH used for precipitation and remained there for 12 h. The filtered chitosan/clay beads were washed by deionized water and stored in the same water. The mean diameter of the beads was 2.5–3.0 mm.

Scanning electron microscopy (SEM)

The structure of obtained chitosan/bentonite composites was studied using scanning electron microscope JEOL JSM-6460 at magnifications from 10^3 to 2×10^6 at 15 kV.

Thermogravimetry coupled with differential scanning calorimetry (TG–DSC analysis)

The thermal decomposition of chitosan/bentonite beads was followed by means of simultaneous TG/DSC using TA Instruments SDT Q600 setup. The measurements were performed employing open alumina crucible and a corresponding empty referent crucible. All experiments were done in the temperature range from ambient temperature to 350 °C in flowing air atmosphere ($100 \text{ cm}^3/\text{min}$) with a heating rate of 20 °C/min. After precipitation, all beads were cut to obtain sample mass about 2.5 mg.

Differential scanning calorimetry (DSC)

The enthalpy changes and glass transition temperatures were measured by differential scanning calorimeter DSC Q20, TA Instruments. The instrument was calibrated using an indium standard. After precipitation, all beads were cut to obtain sample mass about 2.5 mg. All measurements were performed under the nitrogen atmosphere, at the purge gas flow rate of $50 \text{ cm}^3/\text{min}$. The experiments were done from 30 to 225 °C, with a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Figure 2 shows the morphology of three different chitosan/bentonite composite beads. From SEM images it can be seen that beads formed at high NaOH concentration have more irregular spherical shape (sample D), so we may conclude that surface changes of chitosan/bentonite composite beads depend on preparation method and conditions.

Figure 3a presents TG curves of prepared chitosan/bentonite beads. TG/DTG/DSC curves of sample A are presented in Fig. 3b. As the samples were kept under water, the first mass losses up to around 220 °C most probably belong to evaporation of water molecules [25] bonded at different binding sites. The mass loss to 215 °C in all four samples is $13.0 \pm 0.5\%$ meaning that the water adsorptivity of the samples is about the same, regardless to the preparation mode. In samples prepared at lower NaOH concentration the mechanism of water evaporation strongly depends on the bentonite content (Fig. 4a), while in samples prepared at higher NaOH concentration is practically independent of composition (Fig. 4b). The water evaporation and the decomposition of the matrix are not separable, but

Table 1. The code and description of obtained chitosan/bentonite beads (sample name, the volume of chitosan/bentonite solution, the weight content of chitosan/bentonite composites powder, the volume of NaOH solution and the molarity of NaOH solution)

Sample code	Chitosan/clay solution, ml	Chitosan/clay powder, wt.%	NaOH, ml	NaOH, mol/dm ³
A	5	4	10	1
B	3	6	10	1
C	2	5	10	5
D	3	6	10	5

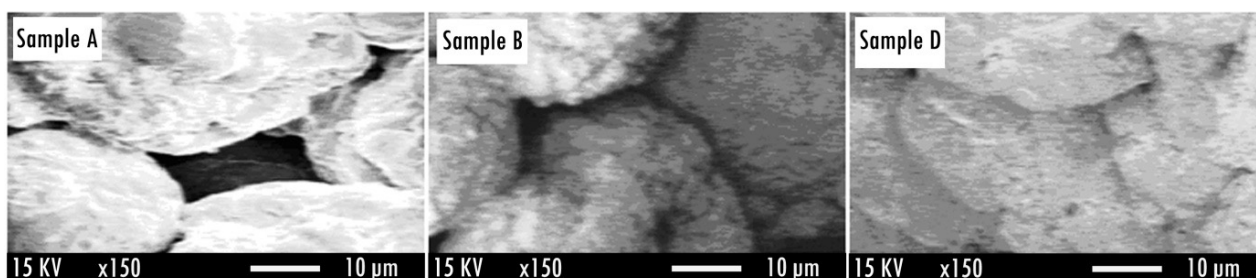


Figure 2. SEM Micrographs of samples A, B and D.

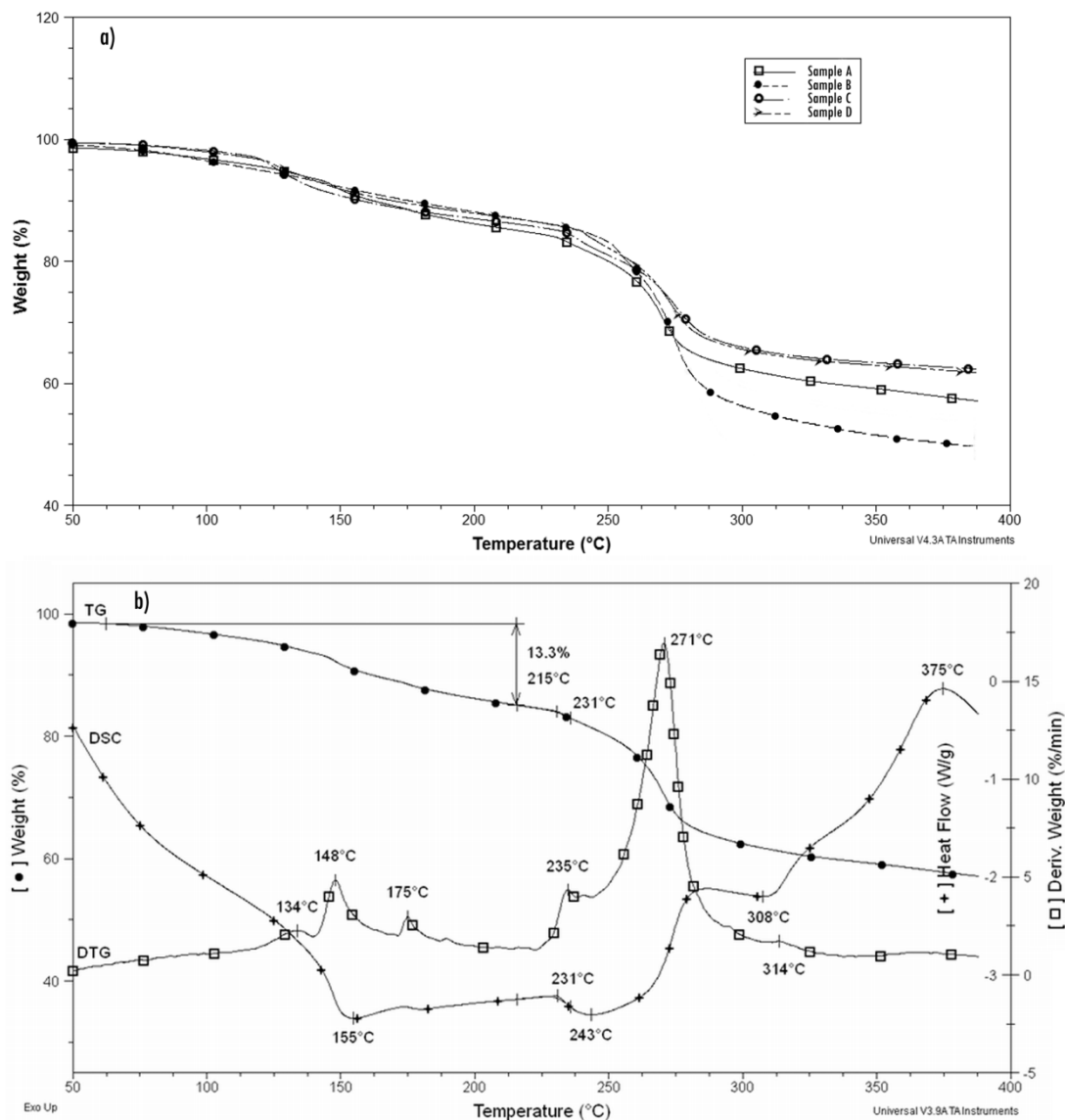


Figure 3. a) TG Curves of prepared chitosan/bentonite beads and b) TG/DTG/DSC curves for sample A.

the decomposition of the matrix probably starts around 230 °C (Fig. 3a).

The processes are endothermic up to ~250 °C (Fig. 3b). Above 250 °C, the decomposition in air is highly exothermic for samples prepared at lower NaOH concentration. The exothermic effects accompanying the decomposition are significantly lower for composites prepared at higher NaOH concentration, in agreement with their more compact structure which prevents the good contact of the beads with air.

As the processes in the whole temperature range are accompanied with mass loss, there is no possibility to determine physical changes in the matrix. However, curves recorded using DSC equipment may be used for a qualitative estimation of the water binding energies (Fig. 5). The glass transition temperature for all chito-

san/bentonite samples was estimated at 144 °C, and it was found to be independent from the preparation procedure. A significantly higher enthalpy change (393.6 J/g) for water evaporation was found for the sample (A), with highest chitosan/clay powder content prepared at lower NaOH concentration. Taking into account the shapes of DTG and DSC curves, as well as the enthalpy values of water removal, it can be concluded that the method of preparation of chitosan/bentonite beads significantly affects their morphology, as well as the interaction of the boundary layer of the solid phase with water. Furthermore, the experimental work is necessary to prove if this observation could be used as a basis for dye removal by chitosan/bentonite composites.

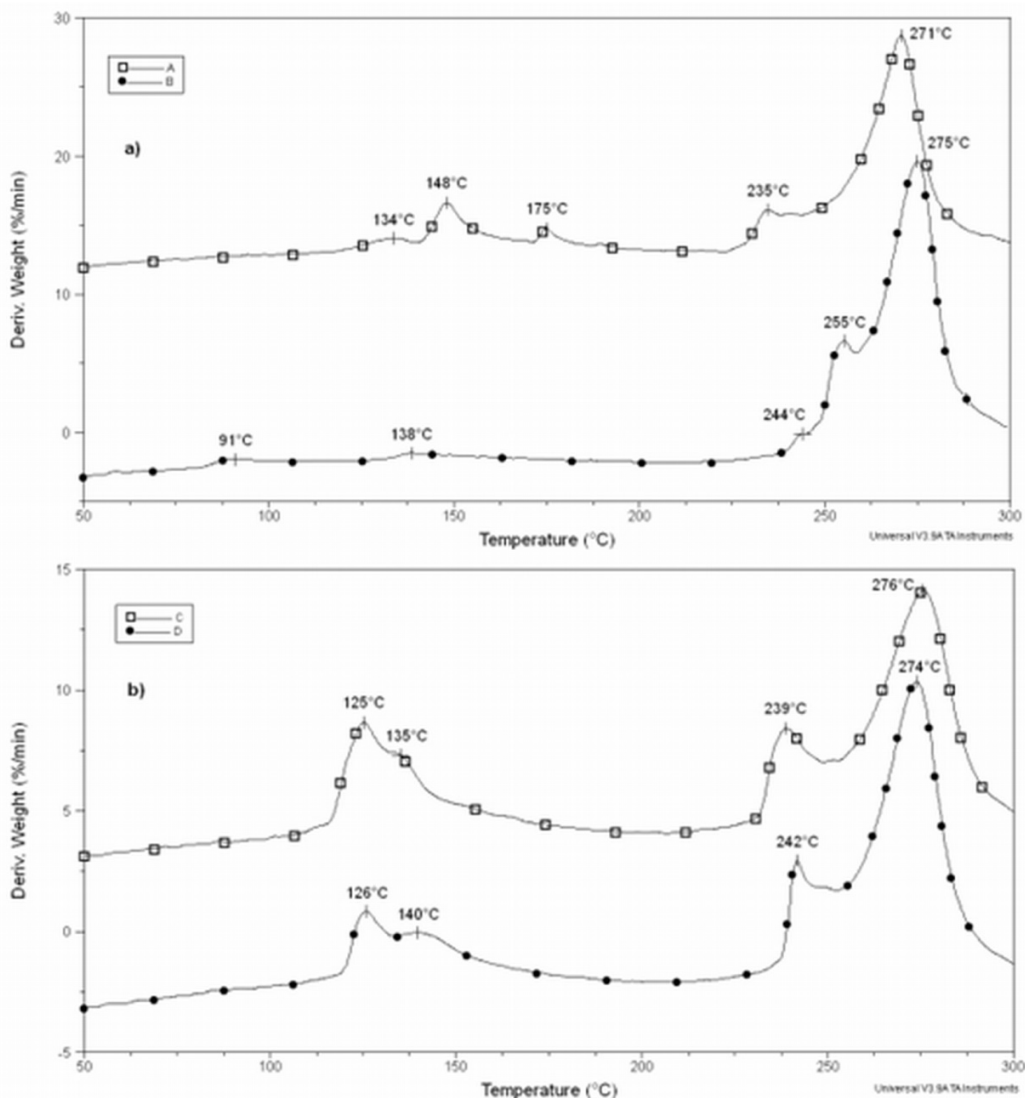


Figure 4. a) DTG Curves of samples prepared at lower (a) and at higher (b) NaOH concentration.

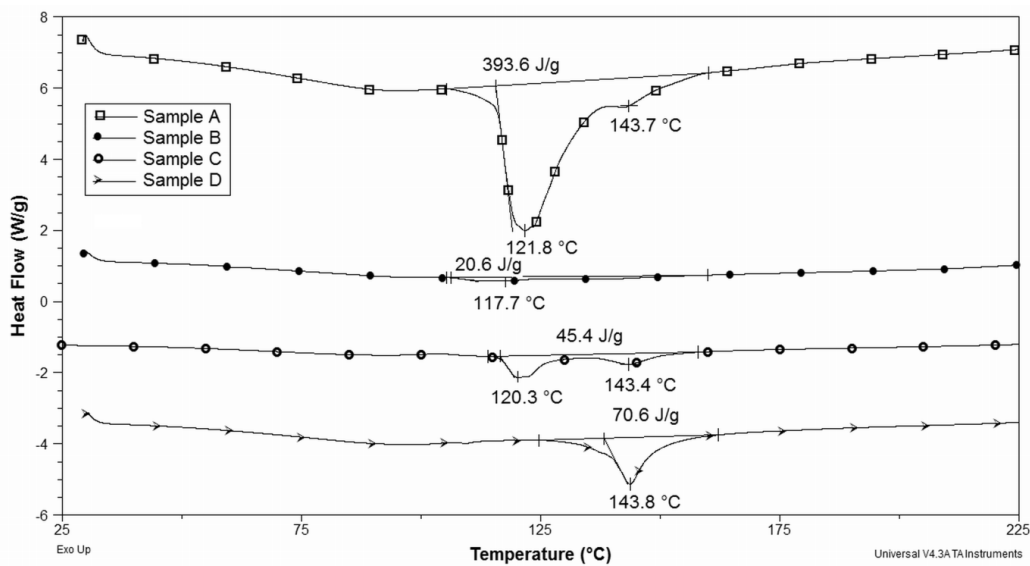


Figure 5. DSC Thermograms of chitosan/bentonite beads.

CONCLUSIONS

This paper was aimed to optimize the preparation procedure of biopolymer/clay composite beads based on chitosan and bentonite intended for wastewater purification. It was found that the preparation procedure affects the morphology and the thermal behaviour of the composites: beads formed at higher basicity of the solution have more irregular spherical shape. The results of thermal measurements refer to the dependence of water adsorption capability on the morphology of the composites. The highest water binding energy belongs to the composite prepared with higher chitosan/bentonite ratio precipitated in solution with lower basicity. The glass transition temperature for all chitosan/bentonite beads was determined at 144 °C.

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IZVOD**DOBIJANJE I TOPLOTNA SVOJSTVA HITOZAN/BENTONIT KOMPOZITNIH GRANULA**

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(Naučni rad)

Zbog biorazgradivosti i netoksičnosti, biopolimerni kompoziti se često koriste kao izuzetni adsorbenti u tretmanu obojenih otpadnih voda. U ovom radu, hitozan/bentonit kompozitne granule dobijene su dodatkom gline u rastvor polimera. Pre pripreme kompozita, bentonit je modifikovan cetiltrimetil-amonijum-bromidom (CTAB). Morfologija granula je ispitana pomoću skenirajuće elektronske mikroskopije (SEM). Toplotna svojstva hitozan/bentonit granula su ispitana istovremenom termogravimetrijom i diferencijalno skenirajućom kalorimetrijom (SDT) i diferencijalnom skenirajućom kalorimetrijom (DSC). Pokazano je da molar-
nost baze (NaOH) koja se koristi za taloženje granula utiče na konačnu strukturu kompozita. Rezultati dobijeni sa TG/DTG i odgovarajućih DSC krivi su pokazali da složeni mehanizam dekompozicije kompozita hitozan/glina zavisi od postupka pripreme uzoraka i da se sastoji od četiri koraka. Uticaj koncentracije baze na razgradnju određen je poređenjem DTG krivi uzoraka sa istim sadržajem praha hitozan/glina, ali različitim sadržajem NaOH. Utvrđeno je da temperatura prelaska u staklasto stanje ne zavisi od postupka pripreme, a za sve uzorke hitozan/bentonit granula je detektovana na oko 144 °C.

Ključne reči: Hitozan/bentonit Kompozitne granule • Termička dekompozicija • DSC