Synthesis and characterization of clay/organoclay-chitosan and clay/organoclay-triethyl chitosan nanocomposites

Kil/organokil-kitosan ve kil/organokil-trietil kitosan nanokompozit sentezi ve karakterizasyonu

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Synthesis and Characterization of Clay/Organoclay-Chitosan and Clay/Organoclay-Triethyl Chitosan Nanocomposites

Highlights

❖ *Syhthesis of chitosan composites and especially modified chitosan (Triethyl chitosan, TEC) composites with improved thermal stability*

❖ *Clays and organoclays formed exfoliated composites with TEC for all clay and organoclay contents*

Graphical Abstract

It was observed that thermal degradation temperature of TEC composites (clay-TEC, organoclay-TEC) increased significantly in reference to composites with chitosan (clay-chitosan, organoclay-chitosan)
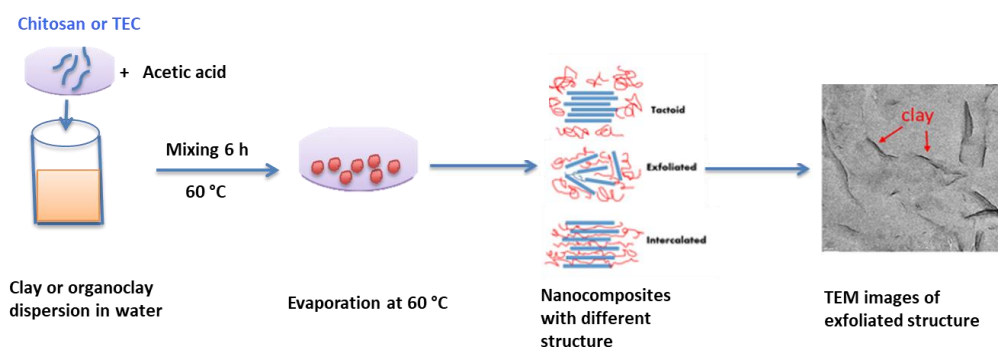

Figure. Synthesis of clay-polymer nanocomposites with different structures

Aim

The aim of the study is to synthesize clay-chitosan, organoclay-chitosan, clay-modified chitosan, organoclay-modified chitosan nanocomposites with improved thermal properties.

Design & Methodology

Purification of clay, Organoclay synthesis, Preparation of triethyl chitosan (TEC), Nanocomposite preparation, Characterization

Originality

To our knowledge, there is no study in the literature on the synthesis and characterization of the modified chitosan-organoclay composites and comparison of compounds type and quantity effect on the composite properties.

Findings

Nanocomposites with TEC showed better thermal stability compared to nanocomposites with chitosan.

Conclusion

The degradation temperature for composites with TEC (965-968 °C) increased significantly compared to composites with chitosan. The results presented a good example for the preparation of chitosan composites and especially modified chitosan (TEC) composites with improved thermal stability.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

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ABSTRACT

Synthesis and characterization of composites, namely clay-chitosan, organoclay-chitosan, clay-triethyl chitosan and organoclay-triethyl chitosan, were investigated by using montmorillonite (Mt) as clay mineral. Cetyltrimethylammonium bromide (CTAB, long-chained)), tetraethylammonium bromide (TEAB, short-chained)), and benzyltriethylammonium bromide (BTEAB, ringed)) surfactants were employed to modify the clay surfaces to obtain organoclay. Organoclays were labelled as CTAB-O (clay modified with cetyltrimethylammonium bromide), BTEAB-O (clay modified with benzyltriethylammonium bromide) and TEAB-O (clay modified with tetraethylammonium bromide). The structural and thermal properties were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). XRD and TEM results showed that exfoliated structure was formed for clay-chitosan composites and also organoclay-chitosan composites at lower CTAB-O, TEAB-O and BTEAB-O content. However, by increasing the organoclay content, tactoid morphology was obtained for organoclay-chitosan composites. Moreover, exfoliated structure was observed for clay-triethyl chitosan (TEC) and organoclay-triethyl chitosan (TEC) composites containing 2.5%, 5%, 10% clays and organoclays respectively. Thermal degradation temperature for 10% clay-chitosan and some organoclay-chitosan composites (5% and 10% TEAB-O-chitosan; 10% BTEAB-O-chitosan) increased (about 375 °C) with regard to neat chitosan (350 °C) at 50% weight loss. Furthermore, it was observed that thermal degradation temperature of TEC composites (clay-TEC, organoclay-TEC) increased significantly in reference to composites with chitosan (clay-chitosan, organoclay-chitosan). In particular, maximum degradation temperature (965-968 ˚C) was reached for clay-TEC (2.5% and 10%), CTAB-O-TEC (5%) and BTEAB-O-TEC (5% and 10%) at 50% weight loss.

Keywords Kelimeler: Clay, chitosan, montmorillonite, organoclay, triethyl chitosan.

Kil/Organokil-Kitosan ve Kil/Organokil-Trietil Kitosan Nanokompozit Sentezi ve Karakterizasyonu

ÖZ

Bu çalışmada montmorillonite (Mt) kili kullanılarak kil-kitosan, organokil-kitosan, kil-trietil kitosan ve organokil-trietil kitosan nanokompozitleri sentezlenmiş ve karakterizasyonları yapılmıştır. Organokil elde etmek için kil yüzeyi uzun zincirli (setil trimetil amonyum bromür (CTAB)), kısa zincirli (tetrametil amonyum bromür (TEAB)), ve halkalı (*benzil trietil amonyum bromür* (BTEAB)) yüzey aktif maddeleri ile modifiye edilmiştir. Organokiller CTAB-O (setil trimetil amonyum bromür ile modifiye edilmiş kil), BTEAB-O (*benzil trietil amonyum bromür ile modifiye edilmiş kil*) ve TEAB-O (tetrametil amonyum bromür ile modifiye edilmiş kil) olarak gösterilmiştir. Nanokompozitlerin yapısal ve termal özellikleri X ışını kırınım difraktometresi (XRD), transmisyon elektron mikroskobu (TEM) ve termogravimetrik analiz (TGA) ile incelenmiştir. XRD ve TEM sonuçları, kil-kitosan kompozitleri ve düşük miktarda CTAB-O, TEAB-O and BTEAB-O organokili içeren organokil-kitosan kompozitleri için dağılmış tabakalı (exfoliation) yapı elde edildiğini göstermiştir. Trietil kitosan kompozitlerinde (kil-TEC, organokil-TEC) ise bütün kil ve organo kil miktarları (%2.5, %5, %10) trietil kitosan içinde dağılarak, dağılmış tabakalı (exfoliated) kompozit yapı oluşturmuştur. %50 kütle kaybındaki termal bozunma sıcaklığı tek başına kitosan için 350 °C civarında iken, 10% kil-kitosan and bazı organokil-kitosan kompozitleri (5% and 10% TEAB-O-kitosan; 10% BTEAB-O-kitosan) için 375 °C civarına kadar artmıştır. Ayrıca, trietil kitosan kompozitlerinde (kil-TEC, organokil-TEC) termal bozunma sıcaklığı, kitosan kompozitlerine (kil-kitosan, organokil-kitosan) göre önemli ölçüde artmıştır. En yüksek termal bozunma sıcaklığına (965-968 ˚C), %50 kütle kaybında kil-TEC (%2.5 ve %10), CTAB-O-TEC (%5) ve BTEAB-O-TEC (5% ve %10) kompozitleri için ulaşılmıştır.

Anahtar Kelimeler: Kil, kitosan, montmorillonit, organokil, trietil kitosan.

1. INTRODUCTION

In recent years, interest in development for polymer/layered silicate composite materials has been growing because the properties of the polymer can be controlled and improved by adding nanoclays [1]. Nanocomposites show excellent properties like improvement in storage modulus, thermal and mechanical properties and ionic conductivity while decrease in gas permeability with regard to pure polymers [2].

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Montmorillonite (Mt) is the most widely used type of clay mineral with two tetrahedral silica layers of Mg or Al [3-5]. The layers are separated each other by a gallery containing ions (Na^+ and Ca^{2+}, etc.) [6]. It is a member of the smectite group consisting of an ''octahedral sheet of aluminum hydroxide'' sandwiched between two silica tetrahedral layers. Mt possesses high ion-exchanger capacities. The imbalance of the negative charges on the surface is eliminated by exchangeable cations (Na^+ and Ca^{2+}).

The association of clay minerals with polymers forms composite materials with different structures such as micro-composite (tactoids), intercalation, and exfoliation as shown in Figure 1 [7]. Different composite structures can be obtained depending on clay nature, polymer matrix and preparation methods.
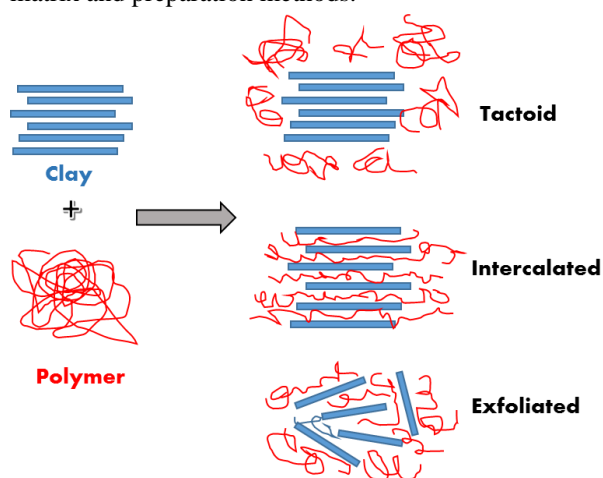

Figure 1. Different structures for clay-polymer materials.

In tactoids, no interaction occurs between polymer and clay layer and clays aggregate in polymer matrix therefore clay particle layers are not separated. Intercalation and exfoliation are two preferred composite structures. If a polymer gets between the clay layers, the interlayer galleries of clay increases and the nanocomposites are called 'intercalated'. When the polymer is introduced into the clay galleries, the well separated clay layers are irregularly dispersed in the polymer matrix, forming 'exfoliated' structure [7].

Most of the industrial applications of clay-polymer nanocomposites are nowadays based on petroleum based polymers. However, expensive petroleum-based polymers are not environmentally friendly and have short-term utilization. Therefore, studies related with biodegradable biopolymers that are derived from natural sources are preferred to petroleum based polymers. Chitosan is a natural polymer with excellent properties such as biodegradability, biocompatibility and bioadhesive properties [6, 8]. Chitosan is nontoxic so it is frequently used in medical applications and pharmaceutical industry. However, properties of chitosan such as thermal and mechanical stability are sometimes not good enough to meet these applications [9]. The incorporation of Mt into the chitosan matrix causes improvement of physical and antimicrobial properties of chitosan, and these improved properties have wide application areas, like electrochemical devices, biomedical applications, water treatment technologies and so on.

The preparation of clay-polymer nanocomposites with tactoid structure is not easy due to the hydrophilicity of clay's surface. Hydrophilic character of clays prevents dispersion of clay minerals in hydrophobic polymer matrix thus, hindering the formation of exfoliated composite with improved properties. Therefore, clay layers are modified with hydrophobic agents to allow the clay layers to be more compatible with hydrophobic polymers. The method used to modify smectites is based on cation exchange with alkylammonium ion and the resulting material is called as organoclays [8]. The most important application of organoclays is to prepare different types of nanocomposites. There is an extensive literature concerning clay/polymer organoclay-polymer nanocomposites [1, 10-12].

Modifying chitosan to improve its solubility in water and other physicochemical properties is also important. Wang et al. [13] studied the controlling of the morphology and properties of chitosan by the combined modification of chitosan and polymer-layered silicate nanocomposites technology (PLSN). They prepared nanocomposites based on chitosan and two different kinds of chitosan derivatives, N,O-carboxymethyl chitosan (CM-CS) and N,N,N-trimethyl chitosan (TM-CS), with Mt. The results showed that modifying chitosan was also important and affected the nanocomposite structure and thermal stability.

To our knowledge, there is no study in the literature on the synthesis and characterization of the modified chitosan-organoclay composites and comparison of compounds type and quantity effect on the composite properties. In this study, clay-chitosan, organoclay-chitosan, clay-modified chitosan, organoclay-modified chitosan nanocomposites were prepared and characterization of their structures were performed with XRD, TEM and TGA techniques.

2. MATERIAL and METHOD

2.1. Materials

Chitosan (deacetylation degree 90%) was obtained from Sigma. Natural clay (Resadiye, Tokat, Turkey) was obtained from Karakaya Bentonit Company [14]. Methylene blue was supplied from Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB), tetraethylammonium bromide (TEAB), benzyltriethylammonium bromide (BTEAB) were supplied from Fluka. Ethyl iodide, N-methylpyrrolidone (NMP), sodium hydroxide and sodium iodide were purchased from Merck.

2.2. Methods

Experiments were performed in four steps: i) natural clay was purified and cation exchange capacity (CEC) was determined ii) organoclay was synthesized [15] iii) modified chitosan was prepared [16] iv) nanocomposite was fabricated [13].

2.2.1. Purification and determination of CEC

Firstly, natural clay (10 g) was put in water (1 L) to precipitate impurities. Then, after 24 h decantation process was performed and the clay-water mixture was filtered for separation of impurities. The centrifugation of clay-water suspension was carried out at 5000 rpm for 15 min. The precipitated clay minerals were separated by filtration and montmorillonite mineral was obtained by evaporating water in a vacuum oven for 24 h. Lastly, the methylene blue test was used for determining CEC of the clay (ANSI/ASTM C837-76) [15].

2.2.2. Organoclay synthesis

The purified clay (10 g) was added in 800 mL water and clay suspension was continuously stirred. The surfactant amount was determined according to CEC value of clay (110 meq/100 g clay), in which it must be 2% higher than the exact amount. Then, surfactant was put in to 200 mL water under stirring to obtain homogeneous solution. After that, homogeneous surfactant solution were mixed by the dispersed clay suspansion and stirred for 4 h. Next, the obtained mixture was separated by centrifugation and washed with water three times. Afterwards, organoclay was dried in a vacuum oven for 48 h to obtain powder. Particles (less than 75 μm) were collected for nanocomposite preparation. This procedure was performed for each surfactants (CTAB, BTEAB, and TEAB) separately [15].

2.2.3. Preparation of triethyl chitosan (TEC)

200 mg chitosan and 8 mL NMP were mixed and the dispersion was stirred for 4 h at room temperature. Then sodium hydroxide solution (1.2 mL), sodium iodide (480 mg) and ethyl iodide (3 mL) were put into chitosan-NMP mixture. The resulting mixture was heated to 60 °C and magnetically stirred for 6 h. The product was precipitated with acetone (200) mL and separation was conducted with centrifugation. The obtained precipitate was added into 4 mL 10% sodium chloride solution and precipitated with 20 mL acetone. The precipitate was dried and TEC powder was obtained [16].

2.2.4. Nanocomposite preparation

Clay-chitosan, organoclay-chitosan, clay-TEC and organoclay-TEC nanocomposites were prepared by an exfoliation-adsorption method. Certain amount of 2 wt %, 5 wt % and 10 wt % clay suspensions were prepared by mixing appropriate amount of clay (or organoclay) in distilled water (100 mL) for 2 h. Then, 1 g chitosan and 1 mL acetic acid 1 mL were put into prepared suspension above at 60 °C under stirring for 6 h to obtain nanocomposites. After that, clay-chitosan and organoclay-chitosan solutions were poured into glass plates, enabling to evaporate at 60 °C [13]. Clay-TEC and organoclay-TEC nanocomposites were prepared similarly.

2.3. Characterization

The resulting nanocomposites were characterized by X-ray diffraction (Rigaku Ultima-IV) with a Cu radiation (λ=1.54 Å). Transmission electron microscope (TEM) was obtained with a Niltramicrotom TEM (300 kV). The thermogravimetric analysis (TGA) was performed using Perkin Elmer Pyris 1 (heating rate: 20 °C/min, atmosphere: N_2).

3. RESULTS AND DISCUSSION

3.1. Structural Analysis and Morphology

3.1.1. Structural analysis of Clay

The clay used in experiment was sodium bentonite (Reşadiye/Tokat) containing 90% montmorillonite and could dispersed water without agglomeration. Table 1 and Table 2 contain chemical analysis and physical properties of clay, respectively.

3.1.2. XRD and TEM analysis

The gallery height in clay particles were determined by XRD. The XRD plots of samples are presented in Figure 2. The reflection peak disappeared with the addition of 2.5%, 5% and 10% clay and 2.5%, 5% organoclays (CTAB-O, TEAB-O, BTEAB-O) to chitosan solution indicating formation of an exfoliated structure (Figure 2a-d). Chitosan has good miscibility with clay because of hydrophilic character, H bonding forms between H on clay and NH_2 or OH on chitosan.

Table 1. Chemical analysis of clay

Compound	amount (%)
SiO_2	62.28
Al_2O_3	17.79
Fe_2O_3	1.68
CaO	4.86
Na_2O	2.70
MgO	1.76
K_2O	1.24

Table 2. Physical properties of clay

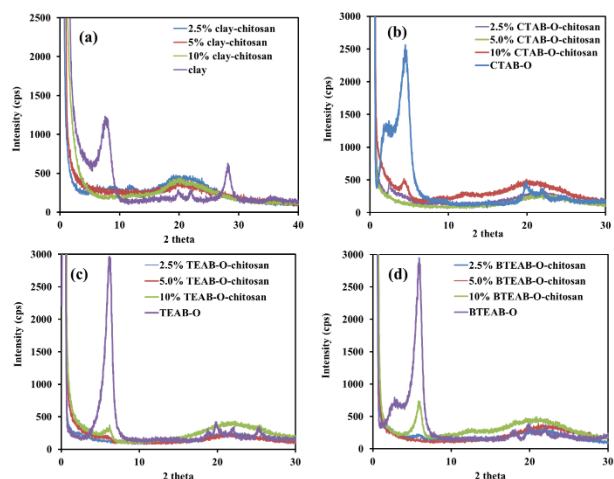| Properties	
moisture (%)	5.0
200 mesh analysis (%)	0.56
600 rpm viscosity (cp)	44
plastic viscosity (cp)	19

Figure 2. XRD peaks for different amount of clays and organoclays a) clay-chitosan b) CTAB-O-chitosan c) TEAB-O-chitosan d) BTEAB-O-chitosan

The clay presents a reflection peak at about $2\theta=7.9°$, corresponding to a basal spacing (d001) of 1.26 nm [9]. The XRD plots of chitosan illustrates characteristic peaks at around $2\theta=10°$ and $2\theta=20°$. After interaction between clay with chitosan, reflection peak of clay at $2\theta=7.9°$ disappeared. Absence of a diffraction peak indicated that exfoliated structure was obtained. Hydrophilic clay could be dispersed in hydrophilic chitosan due to polar interaction. Similar results were obtained by Wang et al. [17]. They prepared clay-chitosan nanocomposites and it was found that the clay showed the existence of intercalated and exfoliated structure at lower clay content. Similar results were also attained for 2.5 wt % and 5 wt % of CTAB-O, TEAB-O and BTEAB-O/chitosan composites. BTAB-O, CTAB-O and TEAB-O organoclays represent characteristic diffraction peaks at $2\theta=5.8°$, 4.4° and 6.1°, attributed to basal spacing of 1.52 nm, 2.01 nm and 1.45 nm respectively. After incorporation with chitosan weak intensity and disappearance of peaks were attained, relating to exfoliated structure at low organoclay contents (2.5 wt % and 5 wt %) in chitosan matrix. However, when the CTAB-O, TEAB-O and BTEAB-O content were increased to 10 wt %, the peak remained at the same position and tactoids occured. This result showed that the chitosan was easily inserted into galleries of organoclay layers for 2.5 wt % and 5 wt % ; however, organoclays were not well delaminated for 10 wt %. due to hydrophobicity of organoclay and limited compatibility between chitosan and hydrophobic organoclay. The formation of intercalation and exfoliation were affected by polar interactions especially due to hydrogen bonding as stated also by Xu et al. [9]. They observed that exfoliated structure was obtained with addition of low amounts (1 to 3 wt %) of nanoclay (MMT-Na) to the matrix. Further increasing to 5 wt % caused both intercalation and exfoliation. In contrast, when they used organoclay (Cloisite 30B), irrespective of amounts, the peaks remained at the same position and tactoids were

formed because of the increasing hydrophobicity of organoclay. It was concluded that, the resulting intercalation, exfoliation, and tactoids structures are related to the amount and type of clay used in nanocomposites.

TEM results are also needed to characterize the structure of the nanocomposites. Therefore, clay-chitosan composites are characterized using XRD and TEM analysis. TEM micrographs of chitosan with 2.5 wt %, 5 wt % and 10 wt % clay are presented in Figure 3.
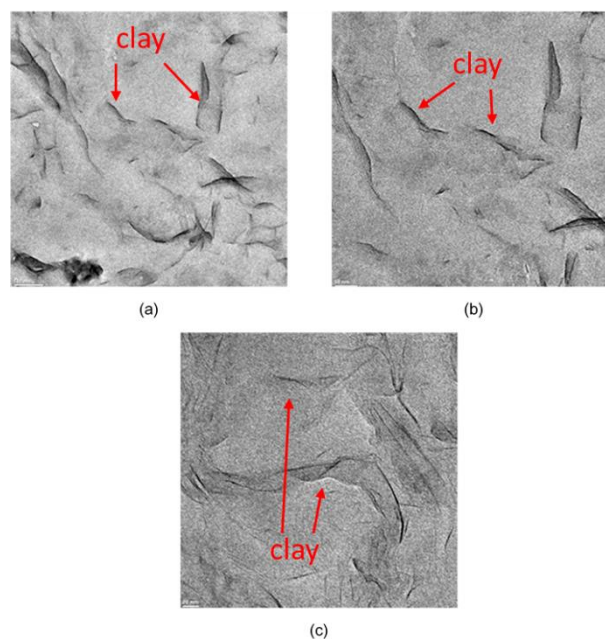

Figure 3. TEM micrographs of a) 2.5% clay-chitosan b) 5% clay-chitosan c) 10% clay-chitosan composites

The dark lines indicate the clay layers in chitosan matrix. TEM image for composites indicated well dispersion of clay in composites. This was verified with the XRD results having an exfoliation structure. TEM images of chitosan nanocomposites containing 2.5 wt %, 5 wt % and 10 wt % organoclays (CTAB-O, TEAB-O, BTEAB-O) were shown in Figure 4-6. It showed exfoliated structure for 2.5 wt % and 5 wt % organoclays that were dispersed in chitosan matrix. However, aggregated organoclays were observed for 10 wt % organoclays in chitosan, indicating the formation of a tactoid structured composites with chitosan. It was thought that for small amount of organoclay, the interlayer distance between layers resulted in exfoliation but further increasing the amount of organoclay caused low compatibility between chitosan and organoclay.

Figure 7a-d shows the XRD patterns of clay-TEC, CTAB-O-TEC, TEAB-O-TEC and BTEAB-O-TEC nanocomposites. Clay and organoclays without TEC shows high crystallinity. However, it was observed that diffraction peaks of all nanocomposites were broadened or disappeared with 2.5%, 5%, 10% clay and organoclays (CTAB-O, TEAB-O, BTEAB-O) addition to TEC. It was inferred that TEC was well dispersed within the

interlayers of clay and organoclays. These results suggested that clay and organoclays (for above mentioned concentrations) were exfoliated in TEC, because disordered structures could not be detected by XRD. Solubility increases in TEC compared to chitosan and exfoliated structure was achieved due to interaction with hydrophilic clay resulting in well dispersion. Although organoclays were hydrophobic, exfoliated structure was also observed for composites with organoclays thanks to polycationic nature of TEC. Similarly, Wang et al. [13] prepared clay and trimethyl chitosan chloride composites and observed exfoliated-intercalated structure together due to quaternized amino cations that could easily move in Mt interlayers.
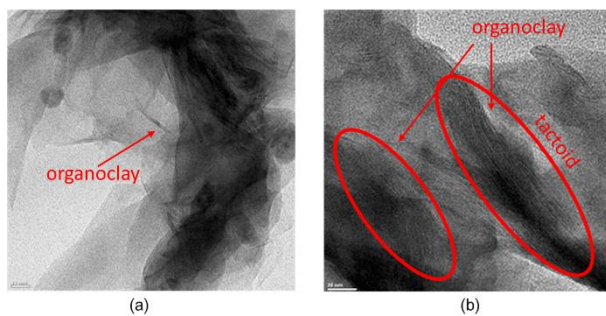

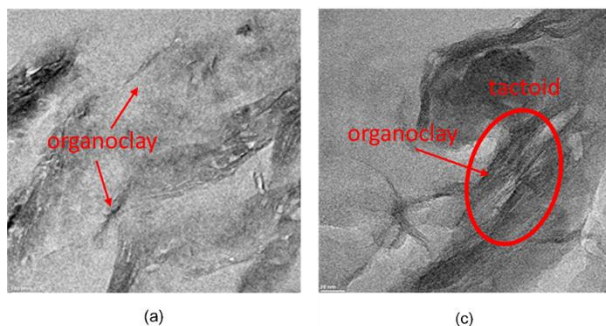**Figure 4.** TEM micrographs of a) 2.5% CTAB-O –chitosan b) 10% CTAB-O-chitosan

Figure 5. TEM micrographs of a) 2.5% TEAB-O-chitosan b) 10% TEAB-O-chitosan
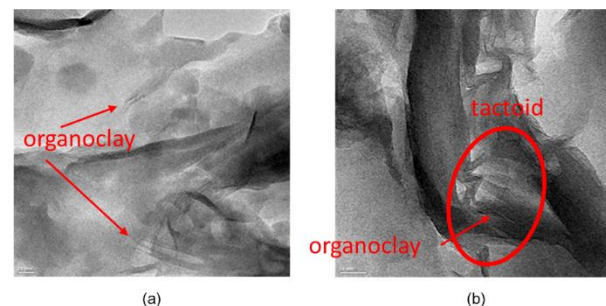

Figure 6. TEM micrographs of a) 2.5% BTEAB-O-chitosan b) 10% BTEAB-O-chitosan

TEM images in Figure 8 (a-d) indicated well dispersed clay and organoclay layers in TEC and it was also confirmed by XRD results. Two phases were observed with dark lines showing the layers of clays and organoclays with irregular shapes. Seams for clay and organoclays were dispersed in TEC and no agglomeration and no tactoids were also sighted. This illustrated that clays and organoclays were well separated in TEC matrix thanks to interaction with TEC, thus resulting in exfoliated structure.
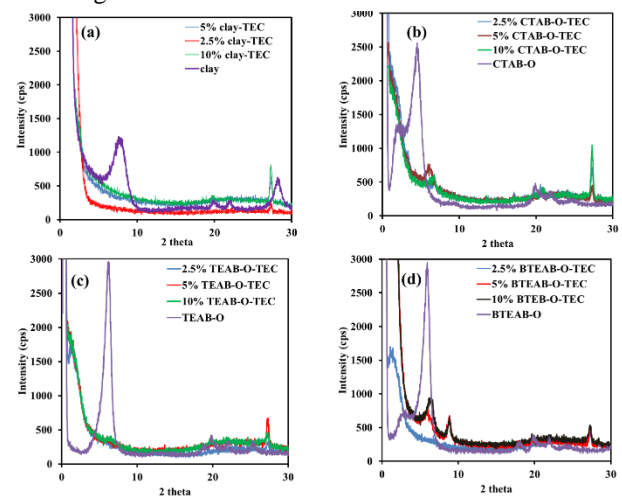

Figure 7. XRD peaks for different amount of clays and organoclays X-ray patterns of nanocomposites with different amount of clays and organoclays a) clay-TEC b) CTAB-O-TEC c) TEAB-O-TEC d) BTEAB-O-TEC
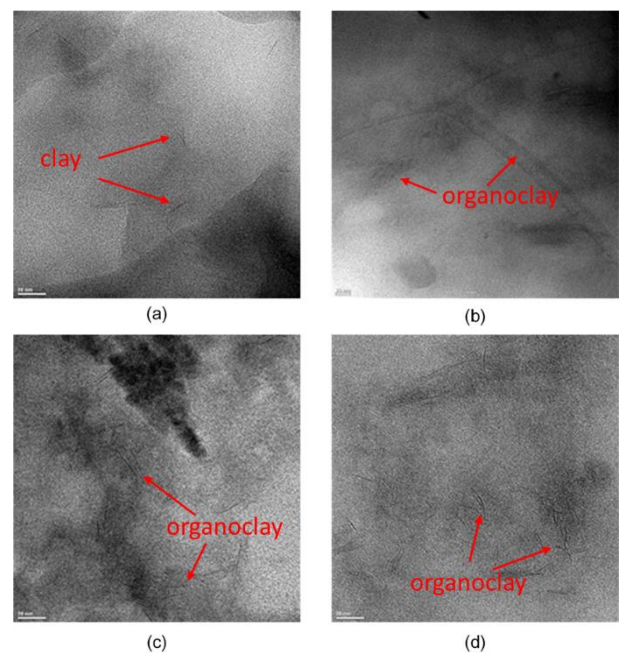
Figure 8. TEM micrographs of a) 2.5% clay-TEC b) 2.5% CTAB-O-TEC c) 2.5 % TEAB-O-TEC d) 2.5 % BTEAB-O-TEC

3.1.3. TGA analysis

TGA plots of clay-chitosan and organoclay-chitosan nanocomposites are illustrated in Figure 9a-d. Generally, thermal stabilities of chitosan nanocomposites increased in contrast with neat chitosan. The weight loss between 50 and 200 °C is due to loss of water and the weight loss between 200 and 450 °C is corresponding to degradation

and deacetylation of chitosan [17].The figures show that weight loss of nanocomposites at higher temperature is slower than that of chitosan. This yields similar results with what other researchers have reported [17, 18]. It was suggested that montmorillonite nanolayers prohibited or minimized the permeability of volatile products formed during decomposition from the composite, therefore the thermal properties of the nanocomposite enhanced [19].
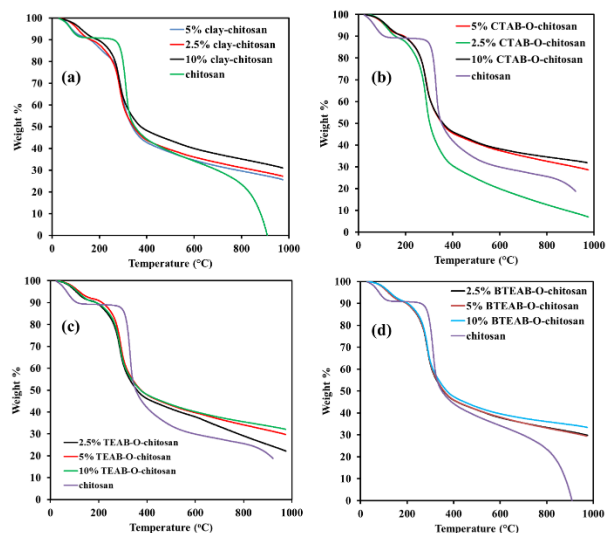

Figure 9. TGA curves of a) clay-chitosan b) CTAB-O-chitosan c) TEAB-O-chitosan d) BTEAB-O-chitosan.

The starting temperature is measured at 10% weight loss and at midpoint at 50% weight loss. Temperatures for degradation of clay-chitosan, CTAB-O-chitosan, TEAB-O-chitosan and BTEAB-O-chitosan are summarized in Table 3.

For all composites starting temperature for degradation is much higher than neat chitosan [9]. The TEAB-O-chitosan composite shows highest thermal stability especially at 10% weight loss (214 °C) compared to neat chitosan (101 °C). The composites, containing 10% clay; 5% and 10% TEAB-O and 10% BTEAB-O content, exhibits weight loss delay at higher temperature (at about 375 ˚C) compared to neat chitosan (350 ˚C) at the

midpoint 50% weight loss. Clays and organoclays in chitosan form heat barrier in chitosan, thus resulting in enhancement of thermal degradation temperature of chitosan by approximately 25 °C at 50% weight loss. Tang et al. [20] prepared chitosan nanocomposites with clay and carbon nanotube (CNT). It was observed that the thermal degradation temperature of chitosan (at 50% weight loss) was enhanced approximately 20-30 °C with addition of 3% either clay or CNT. The degradation temperature for clay-chitosan nanocomposite increased to 387 °C according to neat chitosan (365 °C). In this study, thermal degradation temperature of composites improved to about 375 °C with respect to neat chitosan (350 °C) for 10% clay-chitosan and some organoclay-chitosan composites (5% and 10% TEAB-O-chitosan; 10% BTEAB-O-chitosan) at 50% weight loss.

TGA results for clay-TEC and organoclay-TEC composites are listed in Table 4 and weight loss curves are shown in Figure 10a-d.

It was observed that TEC composites showed lower thermal stability compared to neat TEC. Similar findings were obtained for Mt and terimethyl chitosan composites by Wang et al. [13]. They explained the reason for this temperature decrease as the existence of a strong catalytic effect of Mt on the trimethyl chitosan matrix. Because trimethyl chitosan contained ammonium cations and the thermal decomposition of alkyl-ammonium modified Mt was 200 °C. In this study, it was studied with triethyl chitosan which has a similar structure to trimethyl chitosan. Temperature at 10% weight loss for TEC was measured as 854 °C. The temperatures for composites containing 2.5%, 5% and 10% clay and organoclays changed between 200 °C and 283 °C at 10% wt loss and between 845 °C and 968 °C at 50% wt loss respectively. For clay-TEC and organoclay-TEC composites, about 600 °C temperature decrease was observed compared to neat TEC at 10% wt loss. When clay amount increased from 2.5% wt to 10% wt clay for clay-TEC nanocomposites, degradation temperature rose from 226 °C to 270 °C at 10% weight loss. Similarly, degradation temperature increased with amount of BTEAB-O from

Table 3. TGA data for clay-chitosan composites and organoclay-chitosan

Sample	T at 10% weight loss (°C)	T at 50% weight loss (°C)
Neat chitosan	101	350
2.5% Clay-chitosan	163	344
5% Clay-chitosan	163	342
10% Clay-chitosan	**192**	**375**
2.5% CTAB-O-chitosan	190	359
5% CTAB-O-chitosan	**194**	**355**
10% CTAB-O-chitosan	190	359
2.5% TEAB-O-chitosan	189	358
5% TEAB-O-chitosan	**214**	**375**
10% TEAB-O-chitosan	**189**	**374**
2.5% BTEAB-O-chitosan	197	357
5% BTEAB-O-chitosan	197	358
10% BTEAB-O-chitosan	202	371

Table 4. TGA data for clay-TEC composites and organoclay-TEC

Sample	T at 10% weight loss (°C)	T at 50% weight loss (°C)
Neat TEC	854	---
2.5% Clay-TEC	226	967
5% Clay-TEC	227	921
10% Clay-TEC	**270**	**966**
2.5% CTAB-O-TEC	210	924
5% CTAB-O-TEC	**207**	**968**
10% CTAB-O-TEC	208	910
2.5% TEAB-O-TEC	202	924
5% TEAB-O-TEC	204	892
10% TEAB-O-TEC	204	845
2.5% BTEAB-O-TEC	200	853
5% BTEAB-O-TEC	**283**	**965**
10% BTEAB-O-TEC	**250**	**966**

200°C (2.5% wt BTEAB-O) to 250 °C (10% wt BTEAB-O) at 10% wt loss for BTEAB-O-TEC. There was no markedly change in temperature with the amount of CTAB-O and TEAB-O for CTAB-O-TEC and TEAB-O-TEC composites at 10% weight loss. However, with incorporation of BTEAB-O into TEC, temperature increased from 853 °C (2.5% BTEAB-O) to 966 °C (5% BTEAB-O and 10% BTEAB-O) at 50% wt loss. The maximum degradation temperature for composites with TEC was obtained as 968 °C, significantly higher compared to composites with chitosan in which 375°C was reached as maximum degradation temperature. The degradation temperature decreased for all composites with TEC compared to neat TEC but it was much higher than that of composites obtained with chitosan. For example, degradation temperature obtained for CTAB-O-chitosan composite was 355 °C but it was 968 °C for CTAB-O-TEC composite at 50% weight loss. Therefore nanocomposites with TEC showed better thermal stability compared to nanocomposites with chitosan
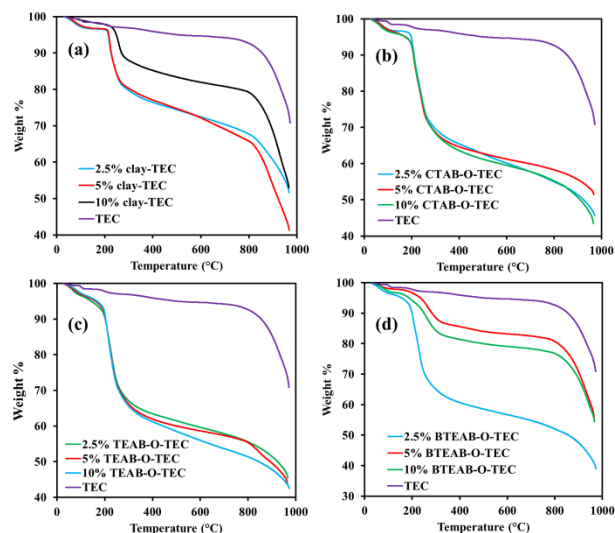

Figure 10. TGA curves of a) clay-TEC b) CTAB-O-TEC c) TEAB-O-TEC d) BTEAB-O-TEC

4. CONCLUSION

The clay-chitosan, organoclay-chitosan, clay-TEC and organoclay-TEC nanocomposites have been successfully prepared. Exfoliated structure was obtained for 2.5%, 5% and 10% clay-chitosan composites and 2.5%, 5% organoclays-chitosan (CTAB-O-chitosan, TEAB-O-chitosan, BTEAB-O-chitosan) composites. However, increasing the amount of organoclays to 10% gave tactoids structure. Furthermore, XRD and TEM results indicated that clays and organoclays formed exfoliated composites with TEC for all clay and organoclay contents. Improvements in thermal stability was achieved for chitosan composites compared to neat chitosan. The degradation temperature for composites with TEC (965-968 °C) increased significantly compared to composites with chitosan. The results presented a good example for the preparation of chitosan composites and especially

modified chitosan (TEC) composites with improved thermal stability. These findings suggest that composites with TEC could be applied to enhance the thermal stability and fire resistance properties of materials. Improved properties of chitosan nanocomposites by nanofiller will extend its application areas. Composites obtained with modification of clay and chitosan structure will provide new research opportunities to develop materials for specific properties.

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DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS' CONTRIBUTIONS

Nuray Çelebi Performed the experiments and analyse the results.

Nuray Yıldız: Performed the experiments and analyse the results.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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