

Effects of different pH medium on swelling properties of 1,2,4,5-benzenetetracarboxylic-chitosan-filled chitosan bio-composites

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Abstract Investigating the swelling properties of chitosan (Cs) film was deemed meaningful, as it plays an important role in predicting the life span of the film. Due to the limits in stability properties, the insertion of reinforcement agent is expected to increase the properties of Cs film. To this purpose, 1,2,4,5-benzenetetracarboxylic-chitosan (BTC) filler was inserted into the Cs matrix. The effect on the degree of swelling (Q_t) and the rate of swelling (Q_r) of the composite film at varying compositions of BTC filler (0, 2, 4, 6, 8, 10 and 12 wt/v%) was investigated. The Q_r and Q_t both decrease with an increasing BTC content, which may be attributed to the looser packaging structure, and the improvement of the hydrophobic character of the composites film. Thus, the addition of BTC filler, up to 10 wt/v%, makes the Cs film more stable with a prolonged swelling time. Meanwhile, electrostatic interaction and hydrogen bonding between the swelling medium and neutral groups, of the polymeric chains of the composites, contributed to the obtained values of Q_t and Q_r . The FTIR results support the argument for the Q_t and Q_r values of different compositions of BTC filler in the Cs matrix, in the different swelling medium (pH 2–14).

Keywords Chitosan polymer · Swelling properties · Bio-composites

Introduction

In recent years, much attention has been focused on the usage of biopolymer materials in food packaging applications, because of their biological functions. One promising biopolymer is chitosan (Cs). Cs is an abundant natural polysaccharide

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that is a deacetylated derivative of chitin and the linear copolymer of β -(1-4)-2-amino-2-deoxy-D-glucopyranose and includes some *N*-acetyl-D-glucosamine residue [1, 2]. As a natural polysaccharide, Cs polymer possesses some interesting properties, such as non-toxicity, high biocompatibility and non-antigenicity. Meanwhile, it has been reported that the usage of Cs polymer in food packaging maintains the freshness of the packed food [3–5]. Nevertheless, drawbacks still exist in food packaging film derived from Cs, such as relatively poor water barrier characteristics [6]. The fact that the Cs film is highly permeable to water molecules limits its usage, which can be an important drawback, since an effective control of moisture transfer is a desirable property of most food packaging [4]. It has also been reported that Cs film is soluble in water, unless it is buffered in an alkaline solution, but the buffering operation leads to substantial film shrinkage [7]. Moreover, Cs film generally degrades quickly in acidic mediums.

It is therefore imperative to develop a stable and durable plastic packaging, using Cs polymer, with controllable permeating or adsorbing properties [5]. Therefore, treatment such as cross-linking [8], blending [5, 9], composites [10, 11], radiation [12] and grafting [13] are used to stabilize the degradation rates as well as increase the life span of the Cs film in various environments. Consequently, forming a biodegradable composite film, with a good compatibility and reinforcement effect in Cs film, is an alternative. For this reason, chemical and physical modification of Cs film has gained interest. The free NH_2 and OH groups of Cs offer great potential for further derivation [4, 13]. Therefore, a variety of chemical modifications, especially the cross-linking approach, has been employed to modify these carbohydrate polymers. On the other hand, covalent cross-linking lead to a Cs system with a permanent network structure, due to the formation of irreversible chemical links. However, the cross-linking process will produce a Cs film with a brittle appearance, which consequently reduces the flexibility of the film [14].

Therefore, incorporation of reinforcement agents into the Cs matrix, using a composite approach, seems to be a better alternative to increase the stability of the Cs film. This idea is believed to limit the non-ideal defects (often non-selective voids) usually occurring in the composite material, mainly due to the poor interaction between the matrix and reinforcement agent phases. From previous studies, the FTIR analysis generally revealed the existence of weak hydrogen bonding interactions, within Cs based bio-composites [1, 10, 15, 16]. Therefore, there is some interest to have a combination of the cross-linked Cs as the reinforcement agent in the Cs matrix, to produce a highly compatible Cs composite system. The introduction of the cross-linked Cs filler not only contributes to good compatibility between composite components but also increases the stability of the produced composites. The cross-linked Cs filler may introduce hydrophobic acyl amine groups, which in turn may lead to a decrease in hydrophilicity and swelling in various mediums, which consequently increases the pore tortuosity of the composite film. Lastly, the degradation of the composites can be minimized and controlled.

Thus, the objective of this study is to check these expectations. The BTC filler was prepared and introduced into the Cs matrix at different filler loadings (0–12 wt/v%). The swelling properties of the produced composite films were examined in various types of swelling mediums (pH 2–14). The swelling process

proceeded until reaching an equilibrium stage, where the Q_t and Q_r values of the composite samples were calculated throughout that region.

Materials

The Cs powder (DD = 85%, $M_w = 200$ kDa) was purchased from Hunza Pharmaceutical Sdn Bhd (Malaysia). 1,2,4,5-Benzenetetracarboxylic was brought from Sigma-Aldrich (Malaysia). *N*-methyl pyrrolidone solvent was purchased from Merck Co. (German) and other chemicals used (NaOH, HCl, distilled water) were all reagent graded.

Methodology

Preparation of the BTC filler

The detailed preparation of the BTC filler was discussed previously [17]. In short, the BTC filler was synthesized from the reaction between Cs powders (2.0 g) with benzenetetracarboxylic monomer (1.58 g) under the N_2 environment, for 6 h at 150 °C, using *N*-methyl-pyrrolidone as the reactive solvent. The reaction mixture was refluxed for 4 h. After that, the final product was filtered off, washed with a methanol/acetone mixture and finally air dried at room temperature. The cross-linked powder obtained was then manually ground into 150 μ m size.

Preparation of composites film

The homogenous dense composite film was initially prepared, using the solution-casting method. BTC filler (0–12 wt/v%) (Table 1) was then dispersed in acetic acid (100 mL, 0.1 M) in a continuous mixing process (2 h, 50 rpm, 35 °C). Cs powder (2 g) was slowly added to the homogenous mixture of BTC filler and acetic acid. Then the film forming mixture (BTC filler, Cs powder) was heated for 2 h at 40 °C.

Table 1 Details on composition of BTC-filled chitosan bio-composites

Composition of BTC filler (%)	Parameter		
	BTC filler (g)	Chitosan (g)	0.1 M acetic acid (mL)
0	0	2	100
2	2	2	100
4	4	2	100
6	4	2	100
8	8	2	100
10	10	2	100
12	12	2	100

The resulting homogenous mixture was allowed to stand for approximately 12 h to remove any air bubbles. The mixture was poured onto a flat level Teflon-coated glass plate. After drying the composite film at room temperature, for at least 72 h, it was peeled from the plate. The composite film obtained was washed thoroughly with deionized water and immersed in NaOH (0.1 M, 500 mL) for neutralization purposes. The neutralization process gave a stronger and greater adhesion at the interface of the BTC filler and the Cs matrix. Dried film was conditioned at 50% RH and 25 °C for 48 h prior to testing. The completed samples were designated as 0BTC, 2BTC, 4BTC, 6BTC, 8BTC, 10BTC and 12BTC, corresponding to the amount of BTC filler content (0, 2, 4, 6, 8, 10 and 12 wt/v%), respectively.

Preparation of the swelling medium

To determine the effects of Q_t and Q_r on different pH mediums (2, 4, 6, 8, 10, 12 and 14), NaCl solutions (obtained from a mixture of NaOH and HCl) with an ionic/cationic strength of 0.0001 to 1 M were prepared. Meanwhile, distilled water was used as the swelling medium of pH 7.

Swelling and degradation measurements

Pieces of composite film (20 mm × 40 mm × 1 mm) were cut and stored in desiccators (0% HR) for 7 days. Samples were weighed to the nearest 0.001 g and recorded as W_{dry} values. Then, the pieces of composite film were immersed in the swelling mediums (pH 2–14) at 37 °C to obtain change in adsorption behaviours, in respect of time. Six samples were measured for each type of composite. After immersing for different periods, the composite films were carefully removed from the swelling medium and (after gentle blotting with tissue paper), were immediately weighed to determine W_{wet} as a function of the immersion time. This procedure attempts to simulate the case of a film applied to a wet surface of different types of pH medium. The percentage of Q_t was calculated using the following equation [14]:

$$Q_t = \frac{1}{\rho_m} \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (1)$$

where Q_t is the degree of swelling, ρ_m the density of swelling medium, W_{wet} the weight of composite film after immersion and W_{dry} weight of composite film before immersion.

The swelling rates (Q_r) of the samples for all tested mediums were calculated from linear regression of the slope, of the steady state period of the curve of Q_t , in sample versus time of swelling (t).

Thickness measurement

The produced bio-composite films' thickness was measured using a digital micrometer [Caliper-Mitutoyo] with a 0.001 mm resolution. The data was taken from several points of the films and an average was calculated.

Fourier Transform Infra Red (FTIR) analysis

FTIR spectra recorded swelling after the composites degradation process. The FTIR spectra were obtained using a FT-IR spectroscopy [FTIR: Perkin Elmer, Model: Spectrum One]. The FTIR spectra were recorded in the wave number range of 4,000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and 4 times scanning in the transmitted mode. The composite film was placed in a vacuum oven in order to dry any moisture adsorbed into the film.

Statistic

All measurements of Q_t and Q_r are the average of five replicates, the results obtained were processed by analysis of variance and the significance was determined at the least significant difference levels of 1 and 5%. The probability $P < 0.05$ means a significant figure and $P < 0.01$ means a highly significant value, as compared to the initial reading.

Discussion

Thickness of the bio-composites

Figure 1 shows the thickness of the bio-composite films, in respect of different BTC filler loadings (0–14 wt/v%). The thickness value increased to 38.9% with the addition of 2–14 wt/v% of BTC filler. It is obvious that the films uniform thickness [with $\delta = 97\%$] was produced over the different ranges of BTC filler content. The thickness effects, due to the addition of the BTC filler, do not follow a particular behaviour pattern. However, at the higher BTC filler loading content (up to 8 wt/v%), the thickness of the composite films was difficult to control.

The thicknesses of the produced composites were not only attributed to different film morphology but they also depended on the nature of the molecules incorporated in their structure [4]. Increasing BTC filler is suspected to result in an increase of film thickness and permeation resistance, thereby the diffusion of water molecules towards the film is hindered.

Proposed interactions of composite components

The compatibility of the Cs matrix and BTC filler can be demonstrated by the performance of a strong chemical interaction between them. Due to the abundant numbers of OH and NH_2 groups of the Cs matrix, and the availability of OH, R–NH and C=O groups of the BTC filler, two types of chemical interactions were proposed to occur at the interfacial bonding of the composite components, inter-hydrogen bonding and electrostatic interaction (Figs. 2, 3). The long chains of the Cs matrix can wind around the bulky structure of the BTC filler and consequently, the entanglement of both macromolecules may easily form both chemical interactions.

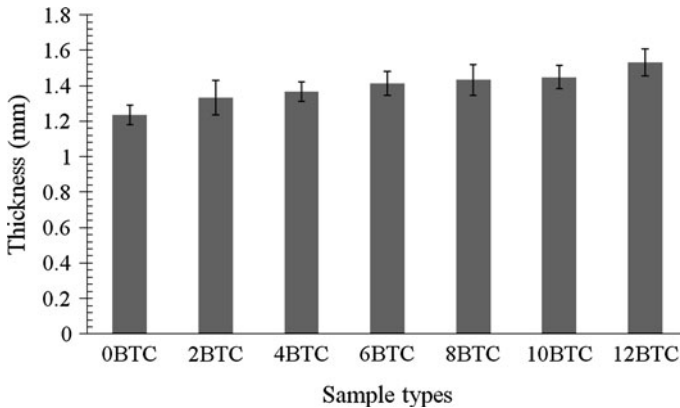


Fig. 1 Variation on thickness of sample which corresponding to difference amount of BTC filler

Generally, the formation of an electrostatic interaction between the composite components, takes place as the Cs matrix is protonated in an acidic medium (solution rich with cationic species) and produces a cationic polyelectrolyte. The reaction takes place with the NH_2 groups of the Cs matrix, since this group is more reactive than OH groups. Meanwhile, the carboxylic anion is formed from the dissociation of protons at the free carboxylic groups of the BTC filler (Fig. 2a). Consequently, the opposite charge of the Cs matrix and the BTC filler will particularly form an electrostatic interaction between those components. Moreover, reaction mentioned will favour heavily towards the conjugate base structure of the Cs matrix, due to the resonance of the carboxylic anion of the BTC filler, with the adjustment of the aromatic rings (benzene ring) (Fig. 2b). Therefore, the pH value of the composite mixtures during the mixing process remained constant. Additionally, the complexes of the BTC filler to the Cs matrix, may be bonded with inter-hydrogen bonding. The OH and NH_2 groups of the Cs matrix will interact automatically with the side groups of the BTC filler (OH, NH and $\text{C}=\text{O}$) to form the inter-hydrogen bonding [11]. Moreover, the CH_2OH groups of the Cs matrix may also form hydrogen bonds with the side groups of the BTC filler (Fig. 3). These interactions may form the basis of a new materials approach, based on the addition of BTC filler into the Cs matrix.

Swelling stage of the sample

Hydrophilicity is an important characteristic property of the biomaterial. To determine the hydrophilicity of the produced composite, the bulk adsorption in different types of swelling mediums (acidic, neutral and alkaline) was determined, to reveal their hydrophilic behaviour. The swelling properties obtained from the hydrophilicity nature of film, can be ascribed as Q_t (degree of swelling) and Q_r (rate of swelling). The ability of the film to expand its physical properties (e.g., weight, dimension) has been introduced into the swollen medium and referred to as Q_t . Meanwhile, the standard terminology used to explain the Q_r is the amount of steady

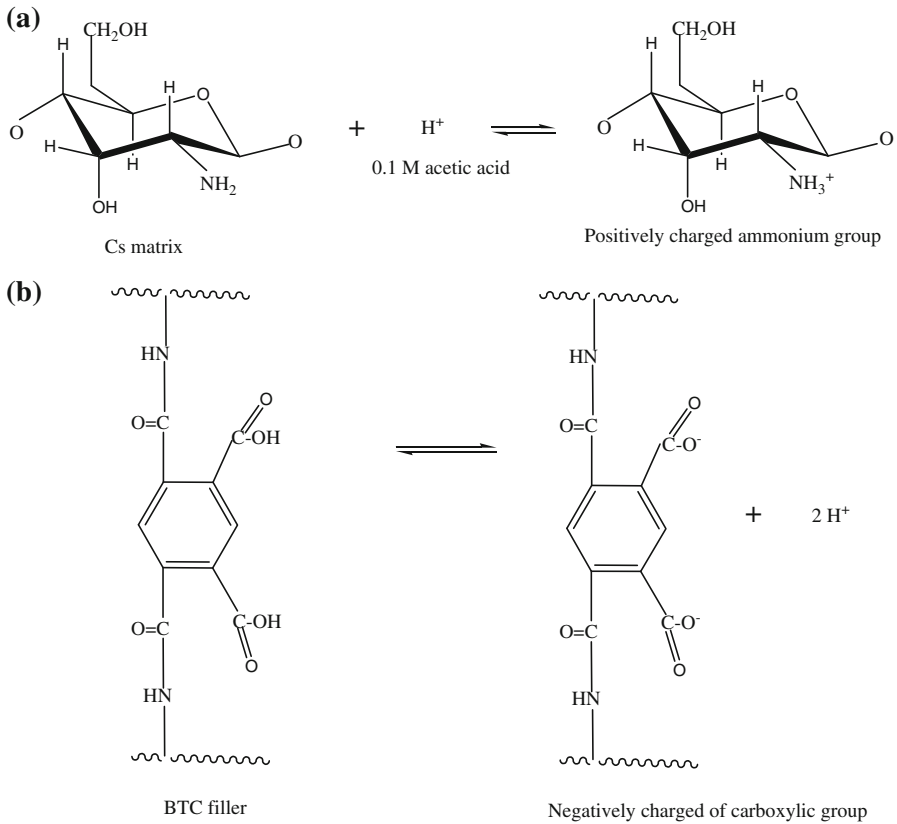


Fig. 2 **a** Formation of conjugate base of Cs matrix (due to the protonization of primary amine groups). **b** Formation of negatively charged of BTC filler (due to the dissociation of carboxylic groups). **c** Formation of electrostatic interaction between positively charged of Cs matrix with negatively charged of BTC filler

water adsorption and unit time through unit area of the immersed sample under the specific condition of temperature and humidity at each of sample surfaces. Additionally, Q_t and Q_r values explain the changes in the polymeric structure, which occur in response to stresses generated within the film during the sorption process.

In acidic medium (pH 2–6)

Figure 4 represents the effects on the swelling properties, of the different compositions of BTC filler, under acidic medium (pH 2–6). The Q_t values were comparatively low for the composite with a greater amount of BTC filler. Generally, all of the samples were able to absorb the swelling medium quickly, at the initial time of swelling (before the equilibrium state) and obtained a positive value of Q_r (Fig. 5a–c). It was observed that with the addition of BTC filler, up to 2–10 wt/v%, the Q_r value of the composites decreased by more than 2–2.5 times (Fig. 5b). In other words, even after 9–12 weeks of contact time, the equilibrium was not reached

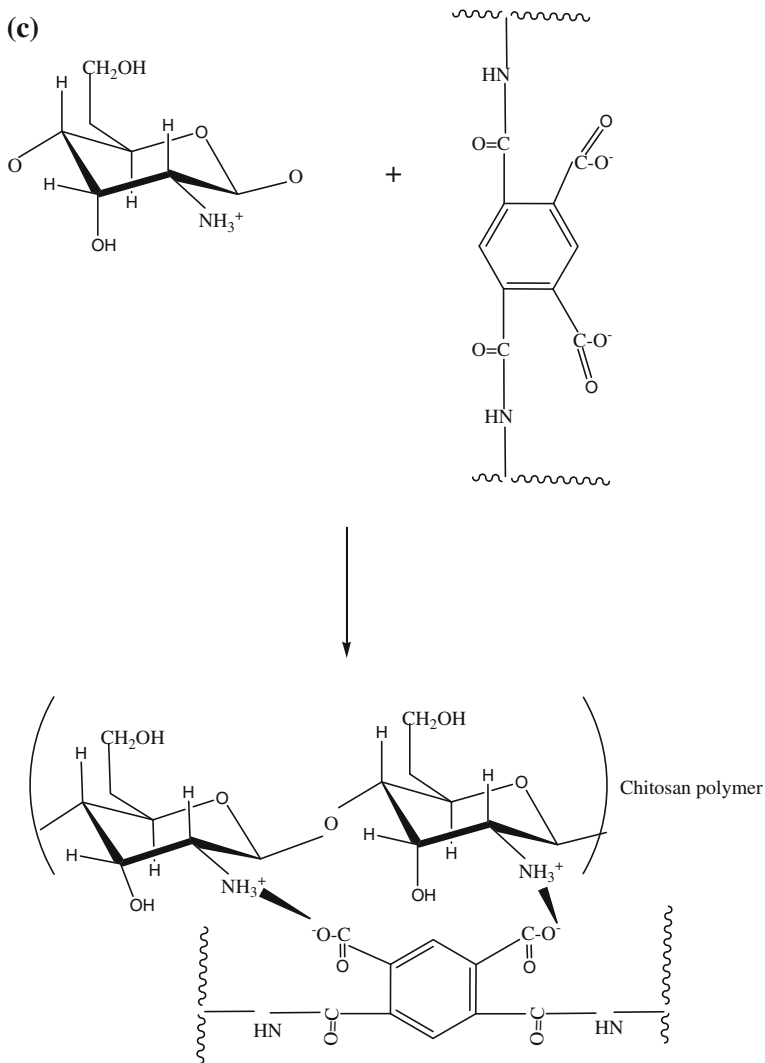
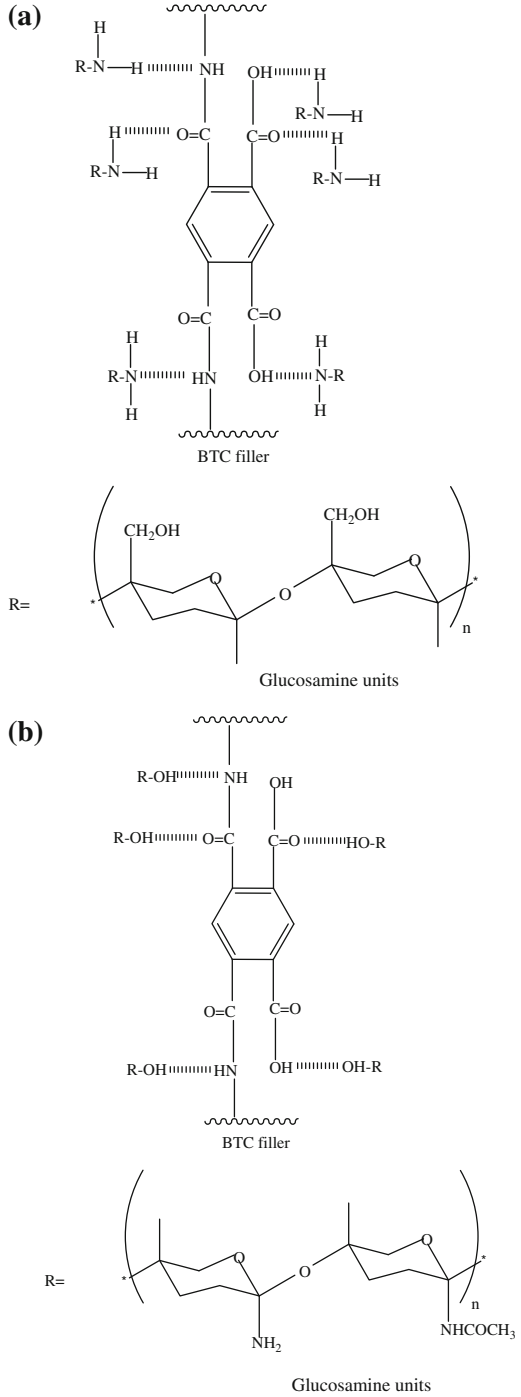


Fig. 2 continued

for composite samples: the approach to equilibrium lasted longer than that of the 0BTC sample (Fig. 5c). After this equilibrium period, the recorded Q_t values did not significantly change with the period of swelling. Meanwhile, the lower Q_r values (at the higher content of BTC filler) were recorded over the range of acidic medium (pH 2–6) (Fig. 5b). The Q_t of 0BTC had similar results in comparison to our previous report [15].

The results obtained can be explained by two main factors. Firstly, was in relation to the number of NH_2 groups in the composite samples. In the presence of H^+ ions, the NH_2 groups of the Cs polymer were able to protonize into

Fig. 3 a Formation of inter-hydrogen bonding between primary amine groups of Cs with polar groups of BTC filler.
b Formation of inter-hydrogen bonding between hydroxyl groups of Cs matrix with polar groups of BTC filler



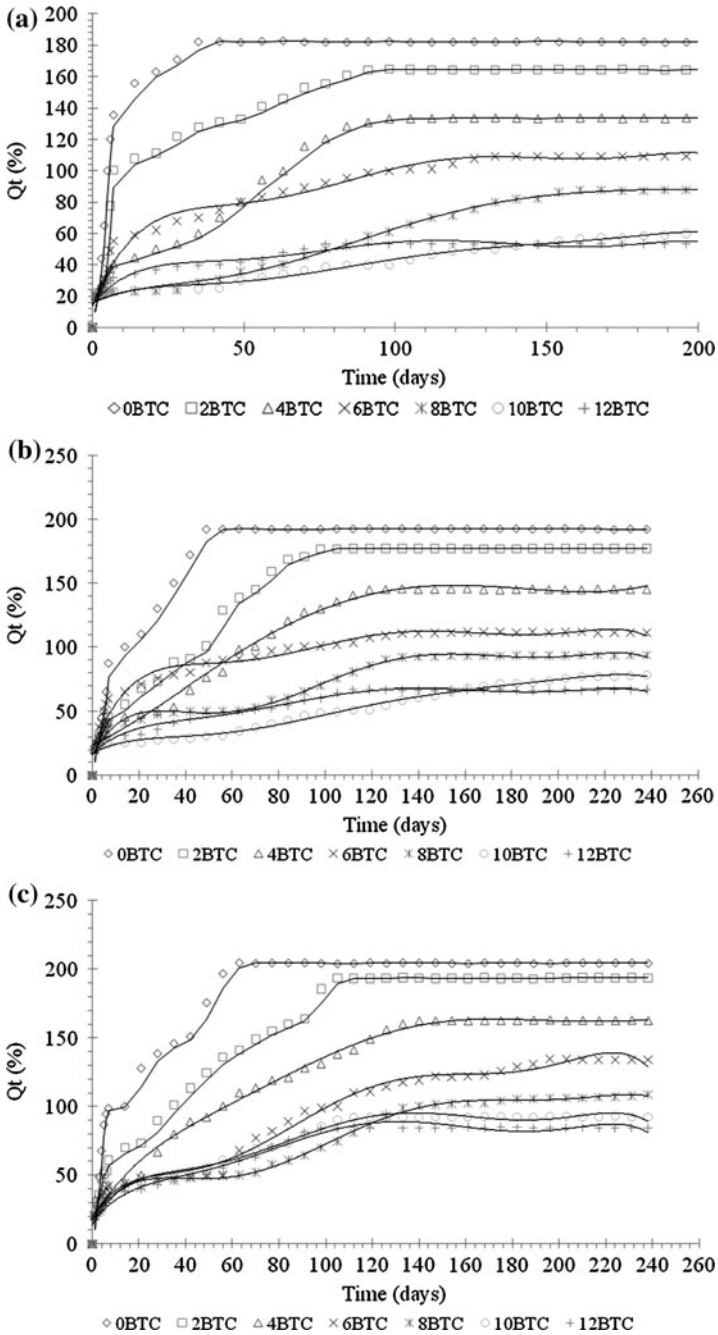


Fig. 4 **a** Swelling profile (Q_t over t) of swollen sample in pH medium of 2. **b** Swelling profile (Q_t over t) of swollen sample in pH medium of 4. **c** Swelling profile (Q_t over t) of swollen sample in pH medium of 6

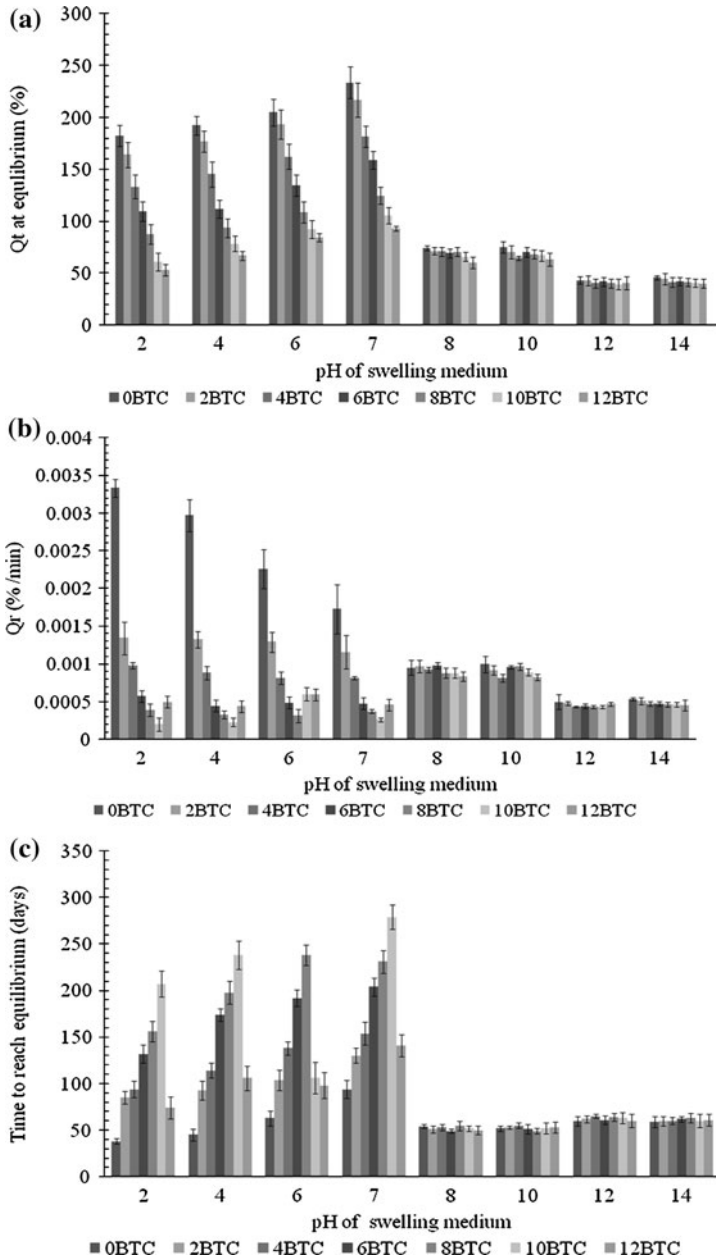


Fig. 5 a Overview of recorded Q_r values on difference composition of BTC filler over difference types of swelling medium (pH 2–14). b Overview of recorded Q_r values on difference composition of BTC filler over difference types of swelling medium (pH 2–14). c Overview of recorded t_{eq} (time to reach equilibrium stage) values on difference composition of BTC filler over difference types of swelling medium (pH 2–14)

NH_3^+ salt [6]. In its protonated form, the Cs matrix exhibited the behaviour of a cationic polyelectrolyte, which was able to dissolve in an acidic medium [7]. Meanwhile, the protonation of NH_2 groups resulting from an acidic pH was expected to promote the electrostatic repulsion of polymer chains and thus the swelling of the film with a possible effect had taken place [9]. Therefore, the addition of 6–8 wt/v% of BTC filler, where only a very few charged NH_2 groups remained in the Cs matrix to be dissolved in acidic medium, since most numbers of NH_2 groups were participating in the formation of either hydrogen bonds or electrostatic interactions with the BTC filler. A smaller number of NH_2 groups present would affect the dissolution and swelling behaviour of composite samples, which would also reduce the recorded Q_t values with the addition of BTC filler. The content ratio of NH_2 on the Cs matrix is, however, higher than that of the BTC filler. It can therefore be inferred, that the higher reactivity of NH_2 groups probably results in a larger protonization process for the composite samples with smaller amounts of BTC filler. Besides, as the number of free NH_2 groups is reduced by addition of BTC filler into the Cs matrix, the produced composite films are less crystalline in nature. The NH_2 groups of the Cs matrix acted as a negatively site for the formation of electrostatic interactions between the BTC filler and the Cs matrix. This electrostatic interaction is stronger than the intra-hydrogen bonds, which are formed in the 0BTC structure. The hydrogen bond can be broken down due to a high pH sensitivity swelling process, whereby higher forces are needed to destroy the electrostatic interaction. Additionally, the accessibility of the remaining groups decreased because of steric hindrance caused by the bulky groups, which were introduced by the BTC filler.

The second factor was attributed to the cross-linked and dense structure of BTC filler. Referring to the structure of BTC filler, the 1,2,4,5-benzenetetracarboxylic cross-linking agent acted as spacers and ties between the chains of the Cs polymer, creating rigid chemical cross links. Therefore, introduction of BTC filler would increase the density properties of the sample, which also attributed to a lower porosity. The adsorption of H^+ ions into the composites structure depends upon the rigidity and extent of polymeric chains, in the composites system. Increasing the density properties would create more difficulties of adsorption, of the H^+ ions into the sample. Therefore, the increase in the amount of BTC filler, the dissociation of ionic linkage between H^+ ions and sample, and the dissolution of the Cs matrix can be limited, leading to a slower adsorption process. It is clear that the 0BTC sample took less than 1 week to be physically robust, while 3 months was taken for the 10BTC sample. Generally, the swelling properties of composite samples results from the various adsorption mechanisms of H^+ ions, the adsorption onto the external surface of the composite, the adsorption on the Cs matrix of the composite, the adsorption on the interface region of the Cs matrix to the BTC filler, and the adsorption on the BTC filler. Therefore, significant increments of Q_t values were obtained during the initial period of swelling and the values were kept constant as the swelling time reached the equilibrium state.

The Q_t and Q_r values of the composites with 12 wt/v% were recorded as the lowest compared to other compositions (Fig. 6a, b). High BTC loading caused the filler to aggregate suddenly. The sudden aggregation resulted in some of the BTC

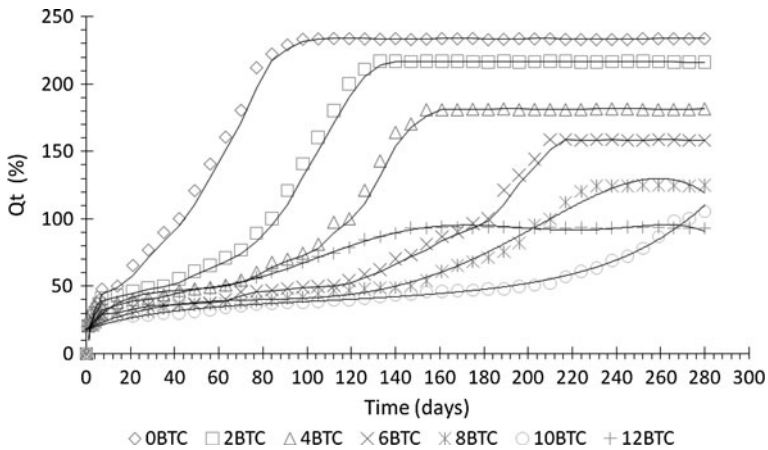


Fig. 6 Swelling profile (Q_t over t) of swollen sample in pH medium of 7

filler touching each other, and inter-hydrogen bonds were easily formed between these BTC particles. Consequently, this makes the Cs matrix become more independent. Therefore, the distribution of BTC filler becomes wider and not as homogenous as in lower filler loadings. The distribution of the pore radius at the contact area of the film and the acidic medium become wider with the Q_t reading significantly increased. At this point, more NH_2 groups of the Cs matrix were protonated and dissolved by the H^+ ions from the acidic medium [6].

As seen in Fig. 5a, the Q_t value of the samples increased linearly with the increase of pH medium (in acidic medium), while the Q_r values reduced in the same pH range. Generally, the changing pH causes a change in the charge density of the H^+ ions within the swelling medium. The sensitive swelling of H^+ ions of the sample was attributed to the change in the charge distribution on the surface of the sample. By increasing the concentration of H^+ ions, the composites swelling properties increase the transported driving force of H^+ ions through the sample. Meanwhile, at a very acidic condition ($\text{pH} < 4$), the carboxylic groups on the BTC filler were converted to a protonated acid form, and hydrogen bonds between them were formed. This resulted in the increase of the samples Q_t values. The pK_a of NH_2 groups of Cs is 6.3, therefore, a pH medium lower than 6.3 will result in an increase to the overall positive charge on the Cs molecules. On the other hand, in a pH medium below 6.3, a more extended molecular conformation of the Cs molecules significantly occurred due to maximum charge repulsion. Within the pH range, the disentanglement of interpenetrated polymeric chains and the destruction of hydrogen bonding between the composites components, which increased the chain mobility, took place, and consequently initiated the samples swelling process. In other words, at a pH below the pK_a of the Cs, the polymer chains are closely lost (due to the destruction of hydrogen bonds), increasing the interaction of H^+ ions with the NH_2 groups of the Cs polymers. The protonization of NH_2 groups leads to the Cs chains repulsion, diffusion of protons and counter ions together with water inside the sample, and the dissociations of the secondary interaction allowing swelling of the samples [2]. This

will expose the functional groups of the Cs polymer and allow interaction with the H^+ ions from the swelling medium. In other words, the higher ionic strength at lower pH acidic mediums, favoured the swelling properties of the samples. Furthermore, certain amounts of Cs matrix dissolve more easily in acidic mediums that contain greater amounts of H^+ ions. This consequently increases the pore size of the composite films and the Q_t values of the films are significantly improved. Therefore, it also shows that the Q_t values, during a constant amount of BTC filler, increases significantly with the decrease of pH values of the swelling medium.

The samples Q_t values reduced slightly as the swelling medium pH exceeded pH 6.3 (Fig. 5a). The reduction was due to the lacking numbers of H^+ ions for the protonization process of the NH_2 groups. Meanwhile, at pHs above the pK_a value, the formation of hydrogen bonds between the Cs networks became significant and allowed the formation of compact polymer networks [18]. However, the reduction of Q_t values occurred insignificantly due to the presence of COOH groups of BTC filler. The COOH groups of BTC filler were gradually ionized to the salt (basic) at the lower concentration of H^+ ions. As the electrostatic repulsed amongst the COO^- groups, an increase in the osmotic pressure inside the sample would take place and allow the swelling of the sample [19]. As the pH rose above 6.3, all COOH groups were converted into salt form, and the optimum Q_t values were obtained. This accounted for similar swelling behaviour in the neutral medium (pH = 7).

The lower Q_r and Q_t values reduced the hydrophilic nature of Cs with the addition of BTC filler, and even the immersion time covered a longer duration. Additionally, the reduction of Q_t and Q_r values at the higher content of BTC filler is beneficial for the application of the composite as a food-packaging application.

In neutral medium (pH 7)

The swelling profile of samples in distilled water is shown in Fig. 6. Generally, the water absorption increases rapidly during the initial time of swelling, while increasing moderately during the intermediate swelling time. With such a large increase in moisture, due to the adsorption of water molecules, the films swell to some extent. The 0BTC composite showed significant differences in Q_t values as being the first one of the highest Q_t . The lowest value of Q_t was obtained from the 10BTC composite. There were significant differences of Q_t values for 4BTC, 6BTC and 8BTC. However, Q_t values obtained for all compositions of BTC fillers were lower when compared to the values from other studies. Meanwhile, the Q_r values are shown in Fig. 6a for Cs composites, in respect of different BTC filler loadings. The recorded Q_r values decreased approximately 15–25% due to the addition of 2–12 wt/v% of BTC filler (Fig. 6b). Based on the recent new findings, there are no reports of swelling properties of native or composite Cs films that can be sustained for more than the duration as found in this present study.

The results obtained could be explained by four main reasons. Firstly, the swelling profile of the samples in distilled water is associated to the polar groups of the composite components. Generally, the main difference between BTC filler and the Cs matrix is that the former contains carboxylic acid (COOH), amide (R–NH–OH), amine (NH_2) and hydroxyl (OH) groups, while the latter contains only NH_2 and OH.

Table 2 Swelling properties of chitosan film in neutral medium from other studies

Types of chitosan	Q_t (%)	t (min)	References
Cs + 61% PEG	2,700	140	[8]
Cs film	750	–	[13]
Cs + PP + AA	1,250	–	[13]
Cs film	45	–	[21]
Cs + 50% QPVP	75	–	[21]
Cs dipping into NO ₂ GAA	110	420	[22]
Cs film	115	1,440	[23]
Cs + 0.6% NaHCO ₃	740	1,440	[23]
Cs + 70 wt% collagen	85	–	[24]
Cs + 70 wt% collagen + 0.7 wt% heparin	100	–	[24]
Cs film	9,000	1,440	[25]
Cs + 5% glycerol	1,500	1,440	[25]
Cs + 50% PEGDMA + HEPK	8,000	1,440	[26]
3% Cs + 10% TPP	45	120	[27]
Cs + PVA + glycerol	3,000	4,320	[28]
Cs + PAAA	13,000	240	[29]
Cs film	350	180	[30]
Cs + Starch	370	180	[30]
Cs + Clay	380	180	[30]
Cs + 0.25 wt% HDI + 50 wt% ethanol	60.2	2,880	[31]
Cs film	70	–	[32]
Cs + 5 wt% CW	68	–	[32]

PEG polyethylene glycol, PP potassium persulfate, AA acrylic acid, QPVP quarternized poly(4-vinyl-*N*-carboxymethyl pyridine), GAA glacial acetic acid, NaHCO₃ sodium alginate, PEGDMA poly(ethylene-glycol)-600-dimethylcylate, HEPK 2-hydroxyl-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone, TPP tripolyphosphate, PAAA poly(acrylic acid-co-acrylamide), HDI hexamethylene diisocyanate, CW cellulose whiskers

Due to the rich hydrophilic groups, such as OH and NH₂ groups on the Cs chains, water molecules can preferentially be adsorbed and diffused in Cs films, through the formation of hydrogen bonding between water molecules of the polar groups of the polymers [20, 21] (Table 2). However, the mechanism for the prediction of water transport through hydrophilic film, such as Cs film, is more complex than the synthetic film. This complexity is due to the non-linear water sorption isotherms and water content, which is related to the diffusivities of the sample [5]. The adsorbed water molecules bind to the hydrophilic sites in the initial swelling process. Cs matrix has more hydrophilic groups compared to BTC filler. Therefore, the water molecules tend to bind with the composite samples with lower amounts of BTC filler through the formation of hydrogen bonding. Previous study reported the stable structure of hydrogen bonds between water molecules and NH₂ groups of Cs polymer. As the water molecules act as providers of protons and the NH₂ groups are the receivers [6, 23, 24], water molecules behave as a plasticizer inside the

composite films. Therefore, the swelling phenomenon would cause conformational changes in the microstructure of the film that not only increase moisture sorption but also creates channels in the polymeric structure allowing an increase in the permanent flow. Therefore, it is believed that during the swelling process, the polymeric chains can move further apart and consequently increase the free volume between the polymeric networks, which finally results in a higher chance of swelling process [25]. It can be seen that at this stage, the Q_t values of the 0BTC sample were recorded as the highest compared to the other samples. During this stage, the obtained Q_r value was also highest, when compared to the other stages. Therefore, there were almost similar responses of Q_r and Q_t performed for all composition of composite films, due to the soaking time effect (Fig. 6).

Secondly, the reduction in water binding capacity of the sample was possibly attributable to a significant interaction between the Cs matrix and the BTC filler (intra/inter-hydrogen bonding and electrostatic interactions), which led to the unavailability of existing binding sites for water molecules within the polymer networks of the sample [20, 26]. The adsorption of water molecules disrupts the intermolecular bonding between the composite components (hydrogen bonding and electrostatic interactions). It is possible, that water molecules are hydrogen-bound to the primary OH and NH₂ groups of Cs, and to the OH, COOH and NH groups of the BTC filler. Therefore, the cross-linked structure of BTC filler provided fewer hydrogen bonding sites and ionic functional residues than the Cs matrix. However, the addition of more BTC content provided extra sites for electrostatic interaction, due to the addition of BTC filler COOH groups in the composite networks. An electrostatic interaction is stronger than hydrogen bonding, therefore, it is more difficult for water molecules to disrupt the composite components which have higher BTC content, since the presence of more BTC content will allow the formation of more electrostatic interactions rather than hydrogen bonding [27]. Consequently, this leads to a decrease in mass ratio of the bound water to the polymer, as the content of BTC filler increased.

Thirdly, the samples adsorption properties towards water molecules were related to the cross-linked structure of BTC filler. Regarding the addition of different amounts of BTC filler in Cs film: the purpose is that the polar side of the BTC filler (OH and C=O) could be bonded to the polar part of the Cs matrix. While the non-polar groups of the BTC filler (benzene ring), was located away from the Cs matrix—creating a better barrier to the water adsorption process. Therefore, the swelling mechanism of composites samples was minimal, stable and controllable in comparison to the 0BTC sample. The different value obtained was most probably due to the different composition of the BTC filler, which reduced the polarity and hydrophilicity of the composite samples. This behaviour did not happen in the linear structure of the Cs matrix, whereas the water molecules interacted directly with the polar groups in the matrix structure causing a plasticization or swelling phenomenon [22, 27]. The phenomenon can be explained as follows: As the water molecules were absorbed into the film with the lesser amounts of BTC filler, the free volume of the film increased linearly with the adsorption, as did the permeability. Consequently, as higher contents of water molecules were adsorbed, the films polymeric structure changed easily. Meanwhile, as the linear network structure was the domain in the composite sample with fewer amounts of BTC filler, a greater amount of water was

trapped in the film, and swelling was promoted. The adsorption of water molecules increased the void size within the composites, and consequently water molecules diffused easily through the film [26, 28]. Therefore, the penetration of water molecules was less permeable in composites with greater amounts of BTC filler due to the reduced free volume and increased penetration energy [29–31]. This might be due to the restricted chain mobility of composite components [2], which were anchored at several points through molecular entanglement with the cross-linked BTC networks, because the fast adsorption behaviour of the swollen sample was based on the freely mobile side chains. These mobile side chains were represented by the free volume of the sample. The free volume of this packed composite film was reduced, by increasing the amount of BTC filler, which gave some difficulties in the adsorption of water molecules.

Lastly, the hydrophilicity of the sample was also associated to the sample thickness [30]. Ideal polymeric films exhibit no thickness effect on the water content of the film. However, as a hydrophilic film, Cs exhibits positive slope relationships between thickness and the water content of the film. Therefore, the 0BTC sample was recorded as having the least thickness (Fig. 1) and the highest Q_t and Q_∞ (Fig. 5a, b). Several explanations have been provided for such anomalous thickness effects to the Cs films, to different structures being formed in the different thickness of films. As the film thickness increased, it showed an increased resistance to mass transfer across it; consequently, the equilibrium of water content at the inner structure of the film was linearly decreased [33, 34]. In the case of the composite samples, the isolated and uniformly distributed water molecules throughout the polymer networks of the samples were greatly dependant on the thickness of the film. The water molecules are adsorbed more easily on a thinner film (the film with lesser amounts of BTC filler). This type of water molecule is named as ‘free bound water’ [22]. The adsorptions of free bound water have greatly restricted the mobility of the polymer networks of the film. Usually, they have strong interactions with the polar and hydrophilic groups of the polymer networks of the film, in the form of ion–dipole, dipole–dipole and hydrogen bonding [26]. Above a certain level of bound water, additional water is preferentially oriented around the bound water and the polymer network structure, as a secondary and/or tertiary hydration shell, which is in a form, generally called a ‘cluster’. This cluster is a cage-like structure, which results from the tendency of water molecules to form the maximum number of hydrogen bonds in the space available [29]. This type of water is called ‘freezing water’. As the sample gradually approaches the equilibrium of Q_t values, the freezing bound water portion becomes more and more predominant. Free water, is the majority that is not involved in the formation of hydrogen bonding with the polymeric structure. The addition of BTC filler reduces the tendency of the sample to easily reach an equilibrium state due to the formation of more free water, in comparison to freezing water, by increasing the thickness of the composite film.

However, as the composition of BTC filler increased to 12 wt/v%, the Q_t and Q_∞ values of the composite film, reduced significantly. This reduction was due to the serious aggregation of BTC filler in this range of composition. The aggregation mechanism was attributed to the highly sticky properties of BTC filler, and the ease that they combined with each other in the excess amount. Therefore, the distribution

of BTC filler, inside the Cs matrix, became inhomogeneous. This led to weakness in the interfacial bonding of the Cs matrix and the BTC filler. With the poor interfacial BTC filler and Cs matrix, the void's size in the composite system became larger and more water molecules had a better chance of diffusing through this void.

The results obtained agreed well with our previous study, which shows that the water adsorbing properties of Cs composites decrease with the increase of reinforcement agents into the Cs film.

In alkaline medium (pH 8–14)

The Q_t value of swollen samples was plotted in an alkaline medium (pH 8–14) as the function of submersion time, as shown in Fig. 7. For a given composition of BTC filler, the Q_t value increased abruptly, with the initial increase in the submersion time, up to approximately 50–64 days, after which the Q_t value increased slowly, which took a longer submersion time (compared to the acidic and neutral mediums) to reach an equilibrium stage. However, dipping in an alkaline solution, over the tested pH for all types of samples, did not give a dramatic swelling behaviour of the sample, compared to dipping in an acidic or neutral medium (pH 2–7). The Q_t over t curve of the 10BTC sample had smoother steps, compared to other compositions of composite curves. Therefore, it is clear that amongst the composite types investigated, the equilibrium percentage of Q_t (at a submersion time of 50 days) of BTC was recorded as the highest (75.11 to 45.66%). Followed by 2 BTC (70.21 to 42.91%), 4 BTC (64.51 to 40.33%), 6 BTC (70.34 to 41.84%), 8 BTC (68.21 to 40.28%), 10 BTC (66.82 to 39.22%) and 12 BTC (62.94 to 40.94%) depending on the pH values of the swelling medium (Fig. 5a). Meanwhile, the samples with lesser amounts of BTC filler reached the equilibrium stage in a shorter time, compared to those with greater amounts (Fig. 7). It is noted that there was no significant difference in Q_t values of swollen samples in mediums with pH 8–10 (Fig. 5a). However, as the pH of an alkaline medium is above 10, it brought a slightly different reduction of Q_t values over the examined samples. Additionally, the Q_t values declined with the increase of BTC filler content, from 0 to 10 wt/v%, but this trend was insignificant as seen in both the acidic and neutral mediums (Fig. 5b). Physically, the composite samples turned slightly fair in colour, as opposed to the brown colour of the control sample. It also can be noted that, increasing the exposure time of sample, lightens its colour.

The cross-linked structure of BTC filler, gives rise to the integrity, physical and chemical stability of the composites, whereas these composite films can minimally swell in an alkaline medium, without disturbing their original frame. Swelling properties of the samples are the result of cohesive and dispersive forces that affect the polymeric chains, resulting in the criterion that determines the stability of the samples polymeric networks [35]. The presence of cohesive force will restrict the adsorption of OH^- ions onto the sample, resulting in a lower Q_t value. The cohesive forces obtained are not only due to the covalent link (cross-linked structure of BTC filler), but can also be related to electrostatic and hydrogen bonds, which take place between the BTC filler and the Cs matrix. The electrostatic interactions play a

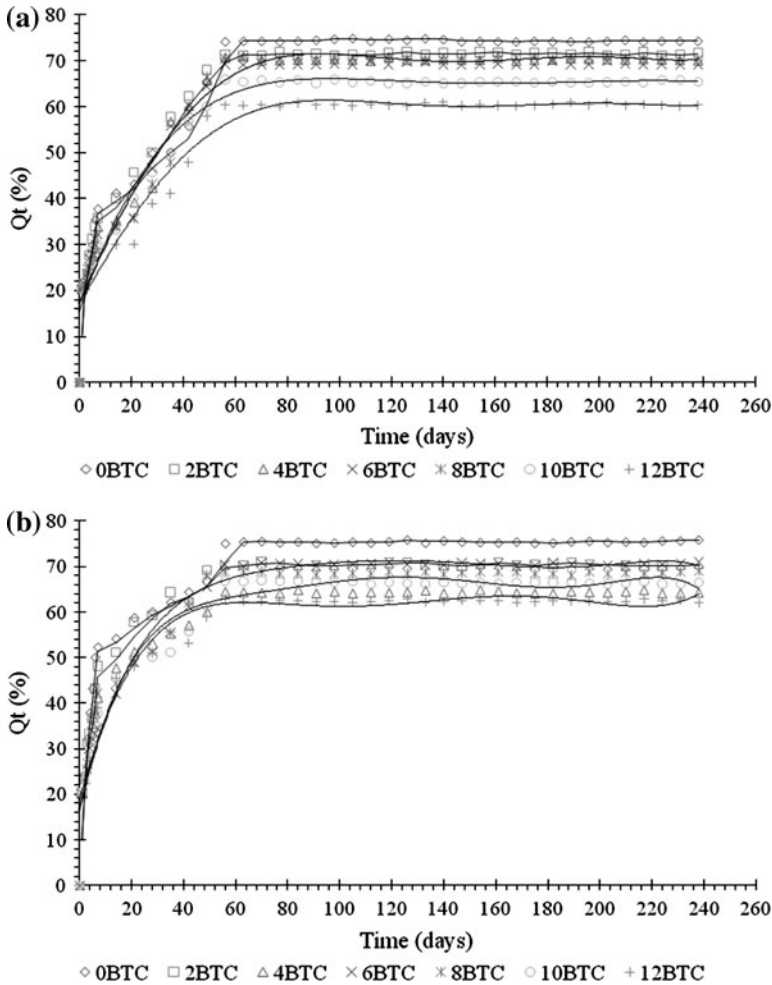


Fig. 7 **a** Swelling profile (Q_t over t) of swollen sample in pH medium of 8. **b** Swelling profile (Q_t over t) of swollen sample in pH medium of 10. **c** Swelling profile (Q_t over t) of swollen sample in pH medium of 12. **d** Swelling profile (Q_t over t) of swollen sample in pH medium of 14

predominant role during the formation of the composite film. It can be deduced that as the ion complexes formation occurred with the electrostatic interaction between RCOO^- ions of BTC filler and the NH_3^+ groups of the Cs matrix, the chain mobility of the composite films could be reduced largely by the ion complex. Subsequently, the resulting films tend to have a more compact structure [26, 36]. Therefore, the electrostatic interaction between the Cs matrix and the BTC filler is reduced during lower contents of BTC filler, as the lower content of Cs polycation is reduced. Furthermore, the compact properties of the sample also attributed to the formation of hydrogen bonding between composite components [28]. As the hydrogen bond interaction was increased, the released parts of polar groups (OH and NH_2) on the

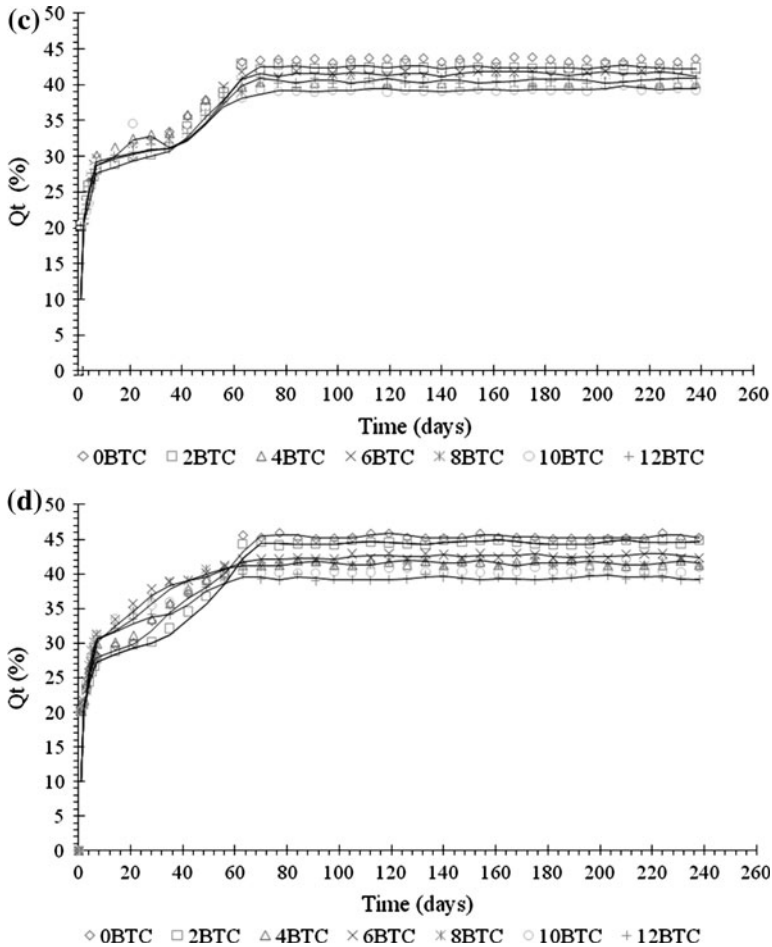


Fig. 7 continued

Cs matrix would decrease simultaneously [11]. This result makes the Cs chains less flexible through the reduction of Cs chain mobility. In this situation, the adsorption of OH^- ions is limited due to the less free volume of the sample. Meanwhile, the hydrogen bonding would aid to stabilize the formation of complex electrostatic interactions.

Meanwhile, the sample Q_t values over the different pH's of alkaline medium, can be related to the changed amount of negative charges on the swelling medium. This behaviour is probably related to the fact that cationic sites remain on the Cs chains to allow electrostatic interactions with the negative charges on the alkaline medium. At pH medium, over 6.3 Cs will be less charged, and will adopt a lesser extended molecular conformation of NH_3^+ [6]. Therefore, the OH^- ions were unable to be completely adsorbed into the composite surface, due to the repulsive effects that occurred between the anionic groups present in BTC filler (due to the dissolution of carboxylic groups) and those present in the alkaline medium. The composite sample

was pulled and shrunk, as the electrostatic mechanism between OH^- and NH_3^+ ions occurred. This mechanism would take place especially during the lower compositions of BTC filler. Meanwhile, during the lower concentrations of OH^- ions, a stronger charge effect on the additional cations was achieved, causing imperfect cations to cations electrostatic repulsion and decreased osmotic pressure difference between the sample polymer network and the external solution of the swelling medium. However, the effect of counter ions, that is Cl^- ions (from the buffer solution of the swelling medium), shielded the charge of cations of the Cs polymer ($-\text{NH}_2^+$ and $-\text{NH}_3^+$) and helped in preventing efficient repulsion. Therefore, the composite films experienced no internal electrostatic repulsive force and could not swell as much as in an acidic medium. As a result, the concentration of OH^- ions (as indicated by the pH of medium) had negligible effects on the Q_t and Q_r values of the composite film. Therefore, the Q_t values decreased slightly with the increment of pH in the alkaline medium.

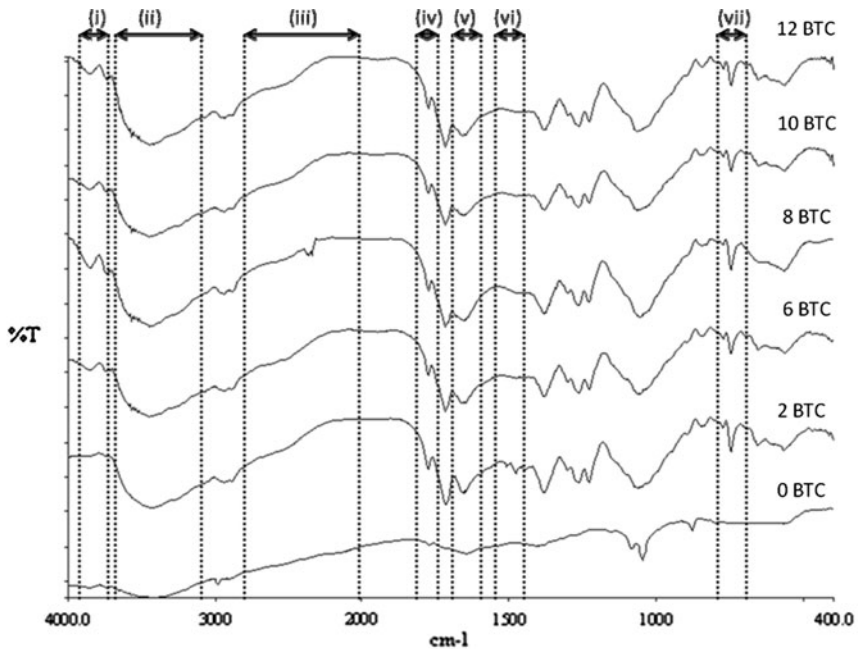
FTIR analysis

FTIR analysis of the sample before swelling process

When two or more substances are mixed, their chemical interactions are reflected by the changes in the characteristic spectral peaks. Addition of BTC filler (2–12 wt/v%) into the Cs matrix, shifted some of the characteristic peaks of the Cs polymer, as seen in Fig. 8. The present peak, at 3,443 and 1,597 cm^{-1} for primary amine $-\text{NH}_2$, decreased with addition of BTC filler, since both of the responsible peaks are used to form the electrostatic interaction with the cationic carboxylic groups of the BTC filler. Besides, a broad peak, around 3,443 cm^{-1} was attributed to $-\text{NH}$ and $-\text{OH}$ stretching vibrations, as well as intermolecular and intra-molecular hydrogen bonding of the Cs matrix to the BTC filler. A weak peak at 2,926 cm^{-1} was from $-\text{CH}$ stretching. The characteristic peaks at 1654, 1597 and 1323 cm^{-1} were assigned to amide I, amine I (NH_2) and amide III adsorption of the Cs matrix, respectively. Meanwhile, the new absorption peaks, at 1,640 and 1,553 cm^{-1} are the $-\text{CO}-$ and $-\text{NH}-$ groups, which represent the amide structure within the BTC filler. At the fingerprint region (at wavelengths from 1,500 to 400 cm^{-1}), the adsorption peak at 1,153 cm^{-1} was significantly performed and assigned to the asymmetric stretching of the $-\text{C}-\text{O}-\text{C}-$ bridge. Additionally, the peaks at 1,075 and 1,033 cm^{-1} were assigned to the skeletal vibration of the $-\text{C}-\text{O}-$ stretching of the Cs and BTC structures. Lastly, a relatively high-intense peak, at around 1,100 cm^{-1} was due to the characteristic polysaccharides peak. Generally, the addition of BTC filler into the Cs matrix can induce a conformational change of the Cs matrix.

FTIR analysis of swollen samples in an acidic medium (pH 2–6)

The influence on the samples chemical bonding changes in an acidic medium was reviewed in the IR spectrum (Fig. 9). Accordingly, under the acidic conditions, electrostatic interaction occurred between the protonated NH_2 and the anionic



Symbol	Wavenumber (cm ⁻¹)	Assignments
(i)	3400 -3500	OH and R-NH ₂
(ii)	3260-3270	C-H stretching
(iii)	3000-2000	No significant peak present
(iv)	1716 -1765	C=O to OH ; C=O to C ; C-O
(v)	1664-1650	C=O to NH
(vi)	1596	R-NH-R
(v)	781	C=O

Fig. 8 Infra red spectroscopy of non swollen sample (0BTC; 2 BTC; 6 BTC; 8 BTC; 10BTC; 12BTC)

COOH groups of the BTC filler, as shown in Fig. 2. For the swollen samples in an acidic medium, the strong and broad absorbent peak, at $3,445\text{ cm}^{-1}$ was divided into two peaks. One corresponded to $-\text{OH}$ asymmetrical stretching vibration, whose changes were insignificant, and the other corresponded to $-\text{NH}_2$ stretching vibration, with which an increase of wave numbers was observed along with the decreasing pH value in the acidic range (pH 2–6). The intensities of these peaks were significantly reduced because of sample swelling process in the acidic medium. Meanwhile, the other NH_2 peak ($1,596\text{ cm}^{-1}$) and amide I ($1,657\text{ cm}^{-1}$) shifted to the peaks at $1,533$ and $1,628\text{ cm}^{-1}$, respectively. Furthermore, the absence of sharp peaks at $1,142\text{ cm}^{-1}$ (C–N) and $1,033\text{ cm}^{-1}$ (C–N) confirmed the interaction of $-\text{NH}_2$ in the Cs matrix, with the H^+ ions, in the acidic medium, forming a complex of NH_3^+ ions. Therefore, the adsorption wave numbers of the C–N stretching vibration and N–H stretching, which were present in the BTC filler structure, were smaller than before swelling process. It was also found that the peaks at $1,117\text{ cm}^{-1}$ ($-\text{C}-\text{OH}$) almost disappeared. These phenomena proved the scissoring of $-\text{C}-\text{OH}$ groups by the H^+ ions in an acidic medium. However, the same adsorbing peaks of $-\text{CH}_2-$ and $-\text{CH}_3-$ groups in the Cs backbone still exist, even after the swelling

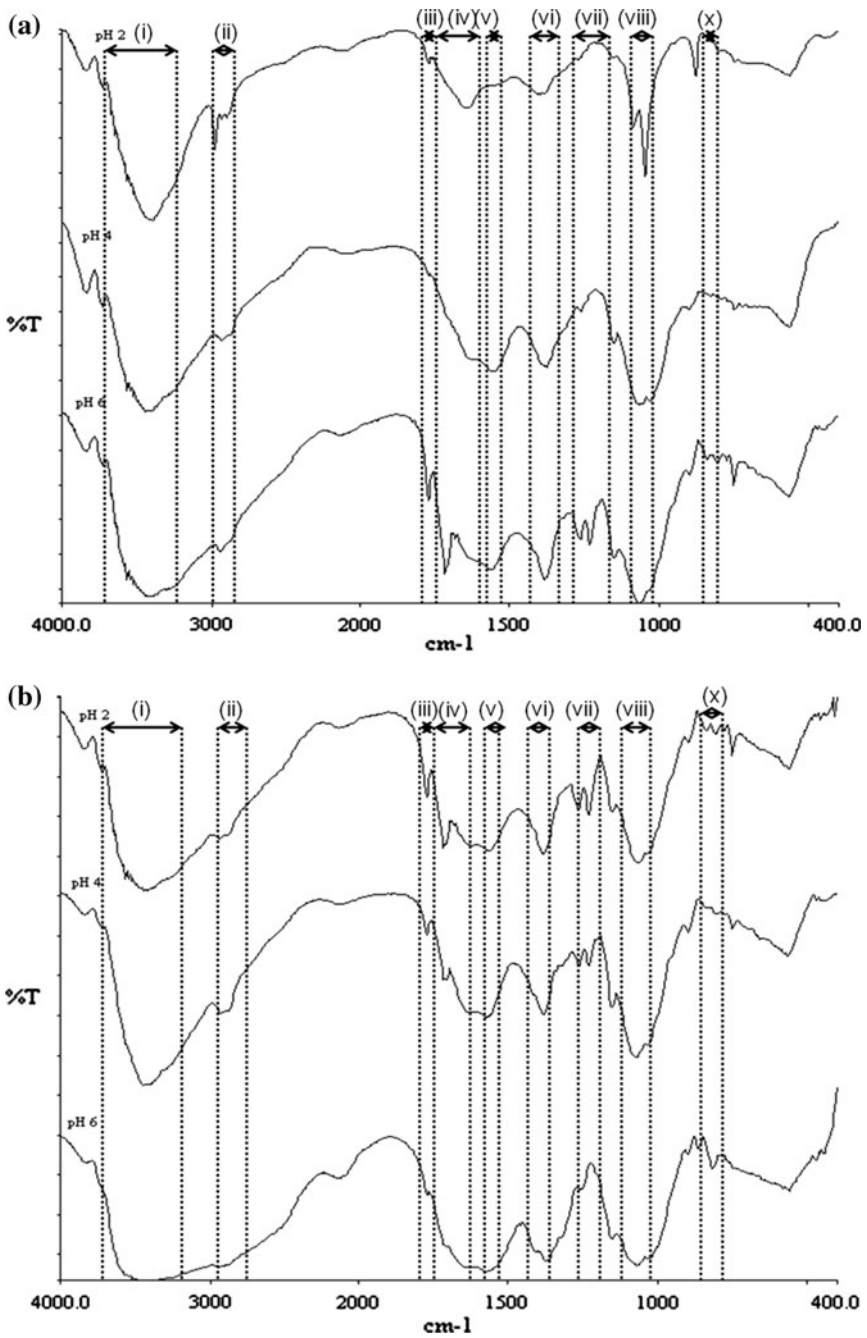
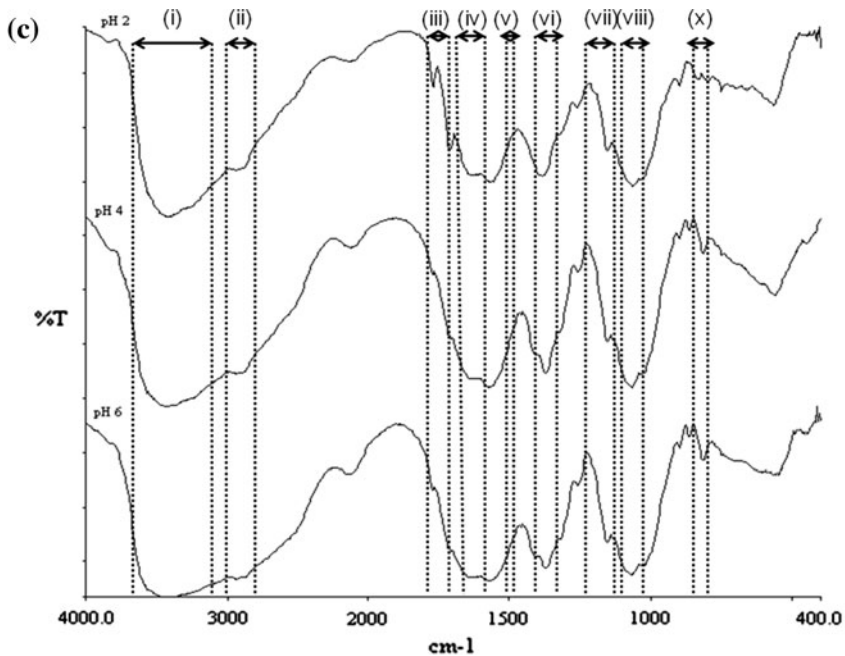


Fig. 9 **a** Infra red spectroscopy of swollen sample in acidic medium (pH 2–6) for 0BTC. **b** Infra red spectroscopy of swollen sample in acidic medium (pH 2–6) for 4BTC. **c** Infra red spectroscopy of swollen sample in acidic medium (pH 2–6) for 10BTC



Symbol	Wave number (cm ⁻¹)	Assignment
(i)	3445	OH asymmetrical stretching ; NH ₂ stretching
(ii)	2877	C-H
(iii)	1719	COOH
(iv)	1657 to 1628	C=O to NH
(v)	1533	NH ₂
(vi)	1403	-COO ⁻ asymmetric and symmetric stretching
(vii)	1142 to 1117	C-OH
(viii)	1033	C-N
(x)	894	-C-O-C- at glycosidic linkage

Fig. 9 continued

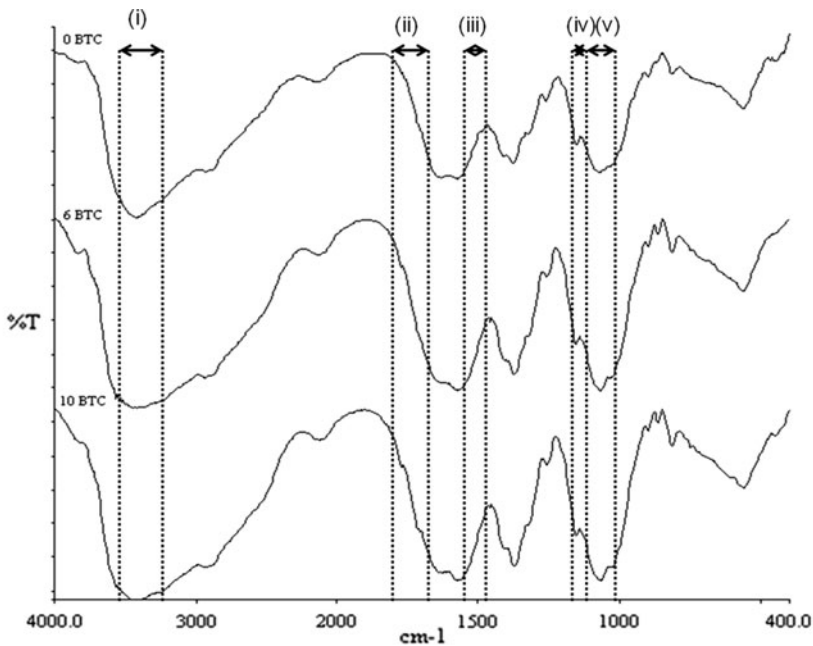
process. However, it can be seen that the adsorption wave number of the $-C-O-C-$ ($1,158\text{ cm}^{-1}$, 894 cm^{-1}) stretching vibration of the 0BTC sample was less significant compared to other samples, which were taken as evidence of the decrease in bond energies of glycosidic linkage in the Cs structure. Therefore, we can conclude that both of the responsible peaks were not involved in the swelling process of the composite films. Additionally, several chemical groups of the Cs structure (OH, C-H and C-OH stretches) were more obviously detected from the swollen composites with lower concentrations of H^+ ions. The most significant is the C-H peak at $2,877\text{ cm}^{-1}$ that became widened, due to the effect of reduction of the H^+ ions. Meanwhile, the peaks at $1,719\text{ cm}^{-1}$ represent the stretching vibration of the $-COOH$ groups and disappeared gradually with the decrease of pH medium (with the increasing concentration of H^+ ions) Consequently, the peaks at $1,567$ and $1,403\text{ cm}^{-1}$ refer to the asymmetric and symmetric stretching of $-COO^-$, which were associated with carboxylic acid salt became significant. Note: the corresponding peaks were becoming invisible in the IR spectra of the swollen sample in pH 6–7. This result

indicated that all of the available carboxylic groups, in the BTC filler, were protonated in an acidic medium (pH 2–4) but ionized at a neutral pH (pH 7), and this confirmed the previous explanation for the samples pH sensitivity.

Generally, the 0BTC sample was easier to degrade than others were. The results indicate that the conformation change of the Cs structure resulted from the dissolution of Cs in an acidic medium, which partially decreases the bond energies of glycosidic linkage in Cs; consequently leading to the whole structure of Cs becoming unstable.

FTIR analysis of swollen sample in neutral medium (pH 7)

As seen in Fig. 10, a broad peak, around $3,443\text{ cm}^{-1}$ appeared for all swollen samples types. The corresponding peak was attributed to $-\text{NH}_2$ and $-\text{OH}$ stretching vibrations, as well as intermolecular and intramolecular hydrogen bonding between the composite components. The reduction of the intensity of the peak at $3,443\text{ cm}^{-1}$, which was associated to $-\text{NH}_2$ and $-\text{OH}$ indicated the disappearance of intermolecular bonding between the BTC filler and the Cs matrix. It can be related to the increment of Q_t values and the swelling time. Simultaneously, the



Symbol	Wave number (cm^{-1})	Assignment
(i)	3443	NH_2 and OH stretching
(ii)	1646	C=O to NH_2
(iii)	1500	NH_2
(iv)	1072	H bonds (water molecules to polar groups of sample)
(v)	1051 to 1026	-C-O-C at pyranose ring of Cs polymer

Fig. 10 Infra red spectroscopy of swollen sample in neutral medium (pH 7) **a** 0BTC, **b** 6BTC, **c** 10BTC

peaks at 1,166 and 1,039 cm^{-1} in the spectrum were replaced by a strong peak at 1,072 cm^{-1} . Such results indicated the presence of water molecules, which disturbing the formation of hydrogen bonding amongst the NH_2 and OH groups of the Cs matrix with the polar groups of water molecules. Meanwhile, the peak at 3,443 cm^{-1} indicates that the $-\text{OH}$ and $-\text{NH}_2$ stretching peaks were shifted to lower wave numbers, presumably because of the association with the adsorption of water molecules, into the composite structure. The shifting can also be detected at peaks of 1,646 and 1,500 cm^{-1} that characterise the amide peak. Therefore, it can be claimed that the BTC filler spectrum is more dominant in the IR spectrum of swollen samples in neutral medium, compared to the IR spectrum of the Cs matrix. A shoulder peak, at 1,657 cm^{-1} in IR spectra of the composite film, before the submersion in a neutral medium (pH 6), was obviously strengthened and blue shifted to 1,664 cm^{-1} , and the peak at 1,596 cm^{-1} is weaker in the sample in acidic medium, compared to the sample immersed in an alkaline medium. The peaks at 1,051 and 1,026 cm^{-1} were the other groups of the Cs matrix pyranose rings and were observed even in the swollen sample during a long swelling process period. Both peaks corresponded to the glucose ring of the Cs structure. Therefore, the presence of these peaks indicates that the Cs structure remained intact after a long swelling process period. Moreover, the characteristic peaks of NH_2 (3,443 cm^{-1}) still appeared in the swollen samples IR spectra.

FTIR analysis of swollen sample in alkaline medium (pH 8–14)

Figure 11 shows the IR spectrum of a swollen sample in the alkaline medium (pH 10) over the range of all examined samples. Under alkaline conditions, the OH groups tend to degrade, as other functional groups, such as NH_2 (1,596 cm^{-1}), amide I (1,657 cm^{-1}), N–H (3,360 cm^{-1}), C–N (1,033 cm^{-1}) and C–N (1,142 cm^{-1}) maintain their adsorption intensity. Therefore, the peak at 1,073 cm^{-1} (C–O of the primary and secondary alcohol) decreases in sharpness. In addition, a small peak of OH appears at 2,922 cm^{-1} . This data confirms that the OH groups of the Cs polymer had changed to become deprotonated OH groups. Besides, the spectrum for the swollen composites, in an alkaline medium, shows a depressed 1,750 cm^{-1} peak, hardly distinguishable from the next 1,657 cm^{-1} peak. Overall, the FTIR spectra for different compositions of BTC filler in the basic medium are very similar. However, at the highest pH medium (pH = 14) the FTIR spectra of swollen composites is slightly different. Meanwhile, as we are unable to compare the spectrum at the same pH, since Cs itself is not soluble in the basic medium, it is difficult to make any firm conclusion about how the structure of cross-linked BTC filler is chemically affecting the structure of the Cs matrix.

Conclusion

The BTC-filled Cs bio-composites have been prepared using the casting technique. The effects on Q_t and Q_r under various conditions of investigated mediums

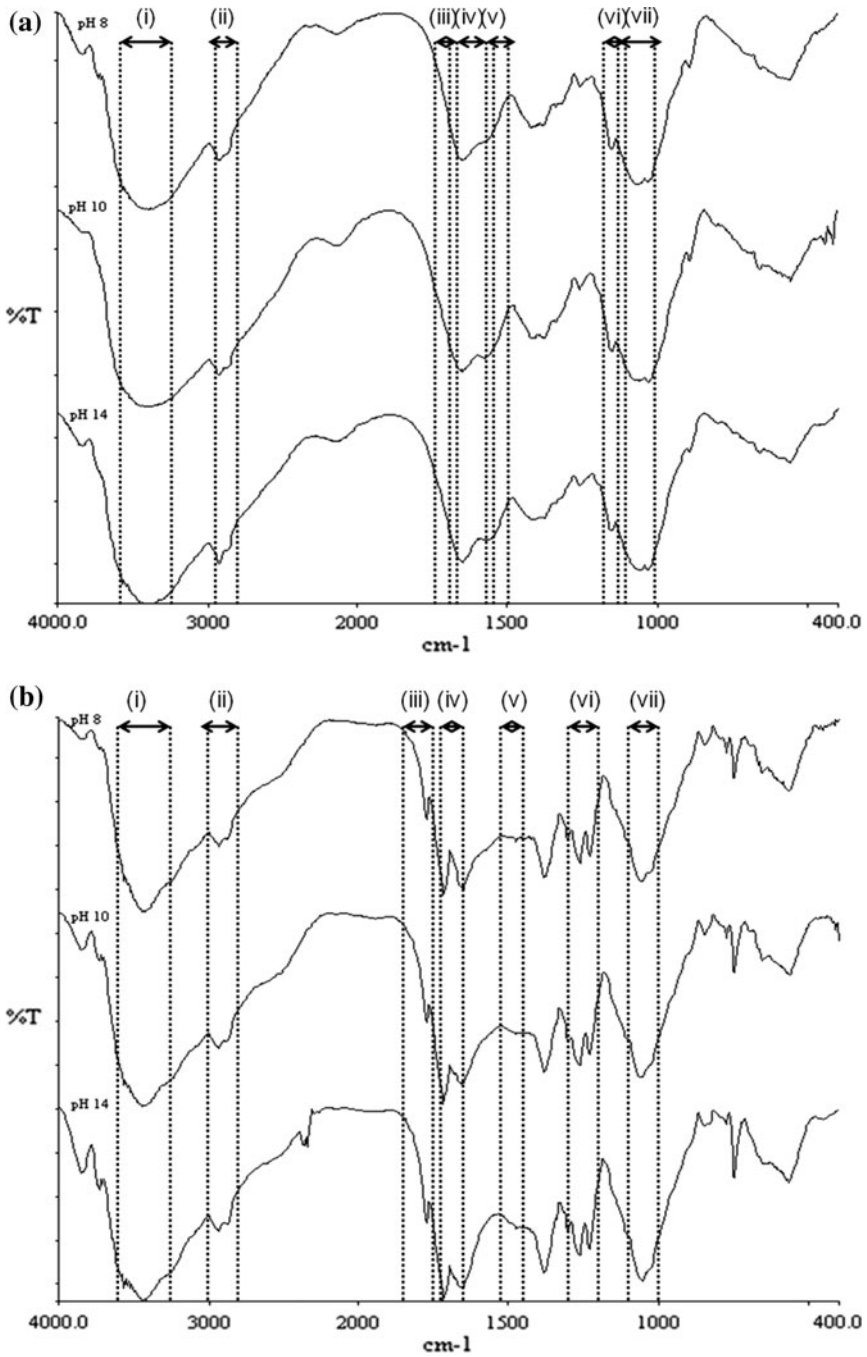
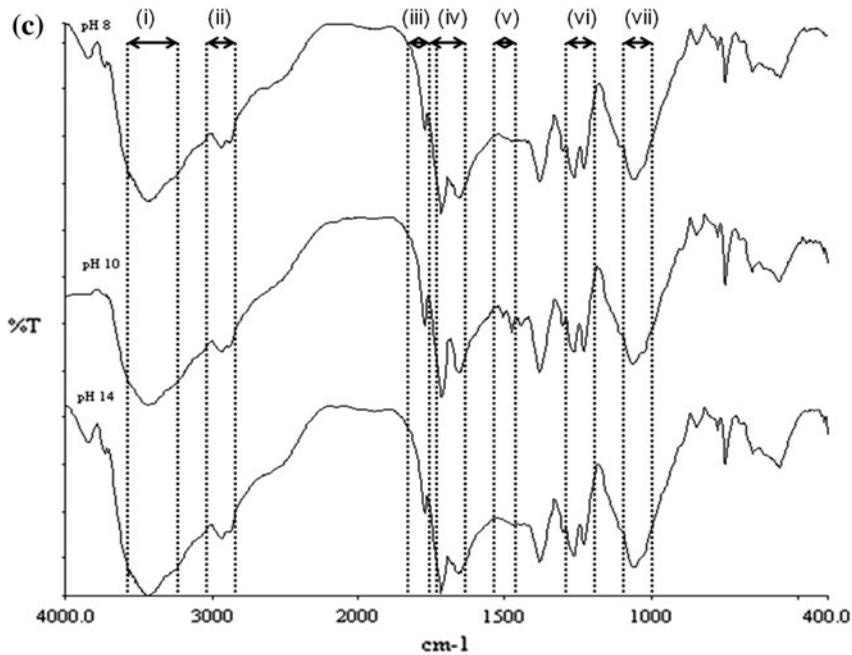


Fig. 11 **a** Infra red spectroscopy of swollen sample in alkaline medium (pH 8–14) for 0BTC. **b** Infra red spectroscopy of swollen sample in alkaline medium (pH 8–14) for 6BTC. **c** Infra red spectroscopy of swollen sample in alkaline medium (pH 8–14) for 10BTC



Symbol	Wave number (cm ⁻¹)	Assignment
(i)	3360	NH ₂ and OH stretching
(ii)	2922	OH
(iii)	1750	C=O to NH
(iv)	1657	C=O to OH
(v)	1595	NH ₂
(vi)	1142	C-N
(vii)	1073	C-O of primary alcohol and secondary alcohol

Fig. 11 continued

(pH 2–14) with different amounts of BTC filler (0, 2, 4, 6, 8, 10 and 12 wt/v%) were studied. The results suggest the following conclusions:

- (1) From the swelling results obtained, the NC film shows greater swelling properties (the highest Q_t and Q_r recorded values), compared to other samples, due to the cationic and strongly hydrophilic water molecules, which interact with the linear molecules structure of NC, and consequently increases the permeation of the water molecules.
- (2) It is required to choose a suitable composition of BTC filler, since composite film from 2 to 10 wt/v% of BTC filler is found to have comparative Q_t and lower Q_r values compared to the 0BTC samples. These results show that Cs composites, with certain amounts of BTC filler, have greater properties of holding more amounts of introduced swelling medium for longer periods, as the swelling process is minimized.
- (3) The values of Q_t increase, with the increase of pH values of buffered medium up to neutral pH (pH 7). Meanwhile, in an alkaline medium, the change of pH

values gives insignificant effect on the Q_t and Q_r values of the sample. The greater Q_t values are probably caused by the greater amounts of hydrophilic groups (cationic ammonium from NH_2 groups of Cs matrix). Besides, the low Q_t value is attributed to the cross-linked structure of the BTC filler.

- (4) The FTIR results of the swollen samples, in all swelling medium (pH 2–14), show that there are coordinating peaks and structures which refer to the break existing in the polymer structure of the Cs matrix and the BTC filler itself.

Finally, these results provide a basis for further study on this kind of plastic packaging material, since low degrees of swelling widen the application of the produced composites film, especially in a highly humid environment.

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