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Synthesis and characterization of hydrogels from cellulose acetate by esterification crosslinking with EDTA dianhydride

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ABSTRACT

Hydrogels were prepared from cellulose acetate with a degree substitution (DS) 2.5 dissolved in dimethylformamide by esterification crosslinking with Ethylenediaminetetraacetic dianhydride (EDTAD) catalyzed by triethylamine. Subsequent conversion of the unreacted carboxyl groups to sodium carboxylates by the addition of aqueous $NaHCO_3$ was performed to enhance the water affinity of the gels. The absorbency of the products was strongly dependent on the amount of EDTAD that was esterified to cellulose acetate, and the highest absorbency was observed for the hydrogel composed of approximately 0.36 molecules of EDTAD per repeat unit of cellulose acetate. The hydrogels were synthesized with different degrees of crosslinking and were analyzed by IR spectral (FTIR), near infrared (NIR), thermogravimetry analysis (TG and DTG), and crosslink density evaluation by Flory-Rehner theory. The hydrogels have synthesized with molar ratios EDTAD/OH groups: [1/1], [1/2], and [0.1/1]. The capacity for water absorbency was studied and compared with the water absorbency of the CA

1. Introduction

The application of hydrogels dates back to 1960, when Wichterle and Lim introduced the use of hydrophilic networks of cross-linked poly (2-hydroxyethyl methacrylate) as soft contact lens material. Hydrogels are extremely suitable for a variety of applications in the pharmaceutical and medical industry. Because they are capable of retaining large amounts of water and because of their soft and rubbery consistence, they closely resemble living tissues. Moreover, their high water content also contributes to their excellent biocompatibility (Vlierberghe, Dubruel, & Schacht, 2011).

Because of the increasing focus on environmental problems associated with synthetic polymers, there is an emerging tendency toward the use of naturally occurring polymers instead of synthetic ones. Among these natural polymers, cellulose, which is composed of (1 → 4)-β-glucopyranose repeating units and forms fibrous structures with high crystallinity, is a prime candidate as a starting material for biodegradable superabsorbent polymers because it is the most abundant biopolymer on earth (Kono & Fujita, 2012).

In principle cellulose hydrogels can be prepared from a cellulose solution through physical crosslinking. Because cellulose has many hydroxyl groups which can form a hydrogen bonding linked network. However, cellulose is very difficult to dissolve in common solvents. Recently, new solvents, such as N-methylmorpholine-N-oxide (NMMO), ionic liquids (ILs), and alkali/urea (or thiourea) aqueous systems have been developed to dissolve cellulose, providing great opportunities for the preparation of cellulose hydrogels. Bacterial cellulose (BC) is also a strong candidate for the fabrication of cellulose-based hydrogels, since certain bacterial species possesses the ability to create pure cellulose hydrogels (Chang & Zhang, 2011).

Cellulose acetate (CA) is a well-known derivative of cellulose and has been used in a broad field of applications such as an adhesive, film base in photography or in separation processes (e.g., filtering, reverse osmosis). Cellulose acetate is produced either by heterogeneous or homogeneous acetylation of cellulose. In contrast to cellulose, cellulose acetate possesses a much less crystalline structure and thus exhibits better solubility in common organic solvents such as acetone (Botaro & Dantas, 2012; Tsioptsias, Sakellariou, Tsivintzelis, Papadopoulou, & Panayiotou, 2010).

In this study, the attention is focused on EDTAD as a croosslinker in the preparation of absorbent polymers from cellulose acetate with DS 2.5. EDTAD has two anhydrides in its structure, each of which reacts quickly with certain functional groups such as hydroxyls to undergo crosslinking. In the reaction of cellulose acetate

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with EDTAD, two free carboxylic acid groups were formed with simultaneous crosslinking of cellulose acetate chains: hence, the absorbency of the product is expected to be enhanced in comparison with that of cellulose acetate. This paper describes a detailed study of the synthesis of hydrogels from cellulose acetate and EDTAD. In addition, the water absorption behavior of the product were investigated to reveal the formation of an excellent absorbent, which is described herein.

This paper aims at highlighting the development in cellulose acetate-based hydrogels with emphasis on the synthesis, characterization, and properties. Recent literature has been cited to summarize work on cellulose-based hydrogel, but, no reports in the literature on synthesis of hydrogel with cellulose acetate and EDTAD.

The hydrogels were analyzed by IR spectral (FTIR), thermogravimetry analysis (TG and DTG), and of the crosslink density was determined from the degree of swelling using Flory-Rehner theory. The hydrogels have synthesized with varying degrees of crosslinking.

2. Experimental

2.1. Materials

The cellulose acetate (CA) with a degree of substitution (DS) 2.5 that has been used in this study was acquired commercially from the RHODIA® group (CA used in the production of cigarette filters). Dimethylformamide (DMF) which has been used as solvent and triethylamine as a catalyst were obtained commercially, both with a purity of 99%. A sample of cellulose acetate, with DS 2.44 and average molecular weight equal to 50.000 g/mol has been used as a standard for the analysis in determining the degree of substitution (DS). This CA was supplied by Sigma–Aldrich®.

CA has been immersed in ethyl ether at room temperature for 1 h and 30 min in ethanol and after it was dried in an oven at 80 °C for 24 h. This procedure has been used to remove impurities from the surface of cellulose acetate. The DMF and triethylamine have been used as received.

2.2. Synthesis of EDTA dianhydride (EDTAD)

The EDTA (disodium salt) (50.0 g) was solubilized in deionized water (500 mL), and then the concentrated HCl was added drop-by-drop until total precipitation of the EDTA (tetra acid). The solid obtained was filtered, washed with ethanol 95%, diethyl ether, and then dried in an oven for 2 h at 105 °C and left to cool in a desiccator. The EDTA (tetra acid) (180 g) was suspended in anhydrous pyridine (310 mL) and then acetic anhydride (240 mL) was added. The mixture was stirred at 65 °C for 24 h. Then the EDTAD was obtained as a solid and was filtered, washed with acetic anhydride, diethyl ether, dried under vacuum, and stored in desiccators (Karnitz, Gurgel, Freitas, & Gil, 2009).

2.3. Hydrogels Synthesis

The CA with DS 2.5 (20 g) was solubilized in 100 mL of dimethylformamide (DMF) at room temperature under vigorous stirring in mechanical stirrer at 300 rpm. The EDTAD was dissolved in DMF at 90 °C under strong stirring. After complete dissolution of the CA and EDTAD, both were mixed with vigorous stirring and were added to 4 mL of triethylamine. The sudden increase in viscosity of the system showed the end of the reaction. The synthesized hydrogels were transferred to a Petri dish and remained for 48 h to cure in desiccators. The gel was milled in a mixer in aqueous medium, filtered and dried in an oven at 75 °C up to constant weight. The preparation of hydrogels from CA was performed in homogeneous medium and triethylamine as an esterification catalyst. The reaction mixture became increasingly viscous soon after adding EDTAD as a crosslinker, and the morphology of mixture gradually changed from solution to gel about 10–20 min after starting the reaction. The hydrogels were prepared from CA according to the scheme presented in Fig. 1.

2.4. Determination of degree of substitution (DS) according to ASTM D 871-96

A total of 0.5 g of cellulose acetate samples was weighed accurately and transferred to a 250 mL flask; to each sample 20 mL of 75% aqueous ethanol was added and then heated for 30 min at 60 °C. Then 20 mL of 0.5 M NaOH solution was added to each sample and again heated at 60 °C for 15 min. The same procedure was also done for a control system (not containing CA). The flasks were stoppered and allowed to stand at room temperature for 72 h. The excess alkali in the sample and control was titrated with HCl (0.5 M) using phenolphthalein as indicator. An excess of acid was added (1 mL) and the alkali were allowed to diffuse from the regenerated cellulose overnight. The disappearance of the pink color indicated complete neutralization of the alkali. The small excess of acid was then back titrated with sodium hydroxide to a phenolphthalein end point (until the solution had acquired faint pink color) (Shaikh, Pandare, Nair, & Varma, 2009).

2.5. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA)

The FTIR spectrum was obtained after grinding the sample into a powder and mixing with KBr powder. The powder mixture was compressed into a transparent disk and scanned from 4000 to 500 cm^{-1} using the average of 32 scans. The Thermogravimetric analysis (TG and DTG) was performed in a synthetic air atmosphere (78% of nitrogen and 22% of oxygen) with a heating ramp of 20 °C/min and maximum temperature of 900 °C.

2.6. NIR spectroscopy

NIR spectra were obtained from the CA, GEDTA12, pure cellulose, and EDTA acid in powder in cuvettes with a front surface window with 32 mm diameter and a depth of 10 mm, on a UV 3600 UV–vis–NIR spectrophotometer (SHIMADZU®), with a spectral bandwidth of 10 nm, 2 nm data interval, and 50 scans per spectrum. The NIR spectra were obtained in diffuse reflectance mode, and afterwards converted to apparent absorbance (A), using the formula A = −log R.

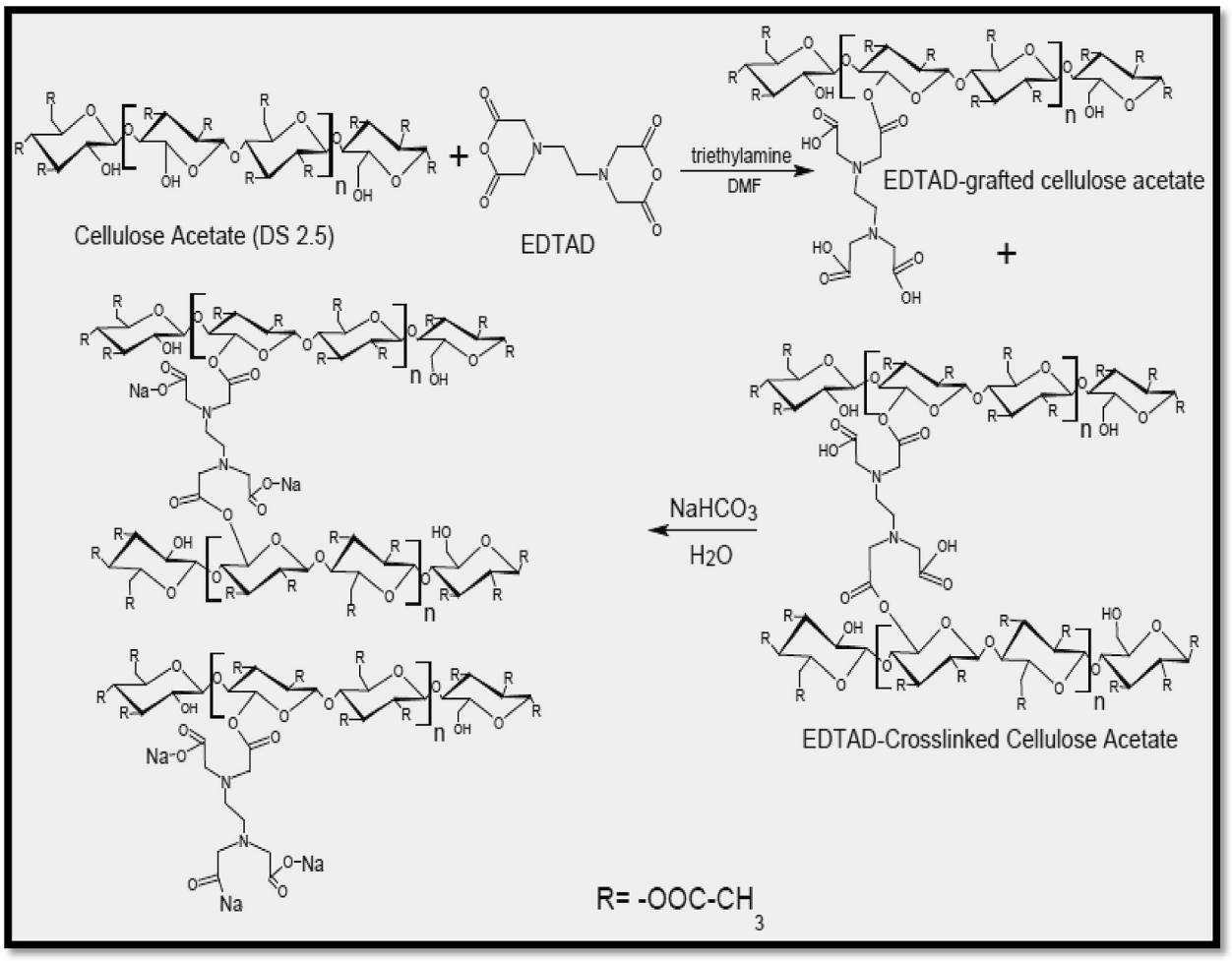
2.7. Determination of crosslinking density

Determination of percentage swelling: The hydrogel was immersed in selected solvents: chloroform [δ = 9,3 $(cal/cm^3)^{1/2}$], acetone [δ = 9,9 $(cal/cm^3)^{1/2}$], ethyl acetate [δ = 9,05 $(cal/cm^3)^{1/2}$], ethanol [δ = 26,2 $(cal/cm^3)^{1/2}$], diethyl ether [δ = 7,4 $(cal/cm^3)^{1/2}$], water [δ = 23,4 $(cal/cm^3)^{1/2}$], and benzene [δ = 9,2 $(cal/cm^3)^{1/2}$], δ is solubility parameter.

Determination of percentage swelling was determined according to ASTM, 1979 and ASTM1239-55. After equilibrium the swollen samples were dried in thermobalance. The percentage of swelling was calculated using Eq. (1).

$$S\% = \left[\frac{(W - W_0)}{W_0}\right] \times 100, \quad (1)$$

where: S% is the percentage of swelling, W is the final weight, W_0 the initial weight.



Nomenclature of Gel	Weight de EDTAD/20 grams de CA	EDTAD mol / mol of free OH
GEDTA11	9,6	1/1
GEDTA 12	4,8	1/2
GEDTA 0.11	0,96	0.1/1

Fig. 1. Reaction of EDTA dianhydride (EDTAD) and cellulose acetate (DS 2.5) in DMF/Triethylamine. Esterification crosslinking and grafting occur simultaneously.

2.8. Determination of total amount of crosslinker in the hydrogels

In this procedure, the tetrasodium EDTA which was produced by the alkaline hydrolysis was titrated with a standard solution of $CaCl_2$. 0.5 g of hydrogels samples was weighed accurately and transferred to a 250 mL flask; to each sample, 20 mL of 75% aqueous ethanol was added and then heated for 30 min at 60 °C. Then 20 mL of 0.5 M NaOH solution was added to each sample and again heated at 60 °C for 15 mL/min. The same procedure was also done for a control system (not containing hydrogels). The flasks were stoppered and allowed to stand at room temperature for 72 h. The solutions were filtered, transferred into 100 mL volumetric flask and completed up to the mark with distilled water; 10 mL was transferred to Erlenmeyers flasks and added 10 mL of ammoniacal buffer pH ~ 10 and indicator Eriochrome black. Then samples were titrated with standard solution of 0.01 M $CaCl_2$ to the end point (color change blue to burgundy).

This titration allowed the weight of EDTA in the polymeric network to be measured. The percentage of EDTA crosslinked and grafted in the hydrogel sample could be determined using Eqs. (2–4):(2)$E_{EDTA} = E_T - Acetyl$,

$$\%Cr = \left[\left(\frac{E_{EDTA}}{mm_{EDTA}}\right) - 1\right] \times 100, \quad (3)$$

$$\%Gr = (100 - \%Cr), \quad (4)$$

where E_{EDTA} is the amount of ester formed by EDTAD and AC (in mmol), *ET* is the total amount of ester (acetate, EDTAD-crosslinked and EDTAD-grafted) in mmol, *Acetyl* is the amount of acetyl in mmol (results obtained from the degree of substitution of CA), *%Cr* is the percentage of EDTAD-crosslinked, *mmEDTA* is the concentration of EDTA in hydrogels in mmol and %Gr is the percentage of EDTAD-grafted.

2.9. Determination of the water absorbency

The hydrogels were immersed in distilled water at 25 and 50 °C, after a prescribed time, samples were collected and filtered

under vacuum. The determination of percentage of absorption was performed with a thermobalance programed with heating up to 105 °C. To calculate the percentage of absorption of water was used Eq. (1). Absorbency measurements were taken for three samples of each product, and the average of the three values was plotted against the absorbency time.

3. Results and discussion

3.1. Determination of degree of substitution (DS) according to ASTMD 871-96

The degree of substitution (DS) of the CA was confirmed. The supplier has indicated DS 2.5 and the result found was 2.56 ± 0.03.

3.2. Hydrogels synthesis

Esterification was allowed to proceed at room temperature for 48 h (cure), and then the reaction product was triturated. Subsequent conversion of the unreacted carboxyl groups to sodium carboxylates in the product by the addition of aqueous $NaHCO_3$ was performed to enhance the water affinity. Finally, the product was purified, washed with distilled water and ethanol, dried, and then screened through a 60 mesh sieve to obtain a white granular product. Samples of hydrogels that were used in the determination crosslinking density, by FTIR and TG/DTG were not neutralized with $NaHCO_3$.

3.3. FTIR analysis

Following the crosslinking esterification reaction of cellulose acetate (DS 2.5) with EDTAD, the obtained product showed several new absorption bands in the FTIR spectrum, in addition to the original peaks from pure cellulose acetate, as shown in Fig. 2. The increase in the absorption band at 1755 cm^{-1} was assigned to the C=O stretching vibration of the carboxylic acid (EDTA acid), and the absorption appearing at 1643 cm^{-1} was assigned to the C=O asymmetric stretching vibration of the carboxylic acid. Formation of the carboxylic acid in the products was also confirmed by the typical absorption at 1385 cm^{-1}, arising from the carbonyl symmetric stretching vibration (Silverstein, Bassler, & Morril, 2005). The IR analysis indicates that the hydroxyl group of cellulose acetate (DS 2.5) may have esterified with EDTAD, resulting in the formation of carboxylic acid as well as crosslinking between the cellulose acetate chains. The results of FTIR corroborate with results obtained by Kono & Fujita, (2012).

Fig. 3.

3.4. NIR spectroscopy

The main differences between the spectra of pure cellulose, GEDTA11, EDTA acid, and CA are in the absorbancies at wavelengths to 1932, 1723, and 1427 nm (Langkilde & Svantesson, 1995). At 1932 nm (characteristic for ($RCOOR_1$) and ROH vibrations), the explanation for the higher absorbance of the CA, is the proximity of the polymeric chains due the hydrogen bonding between the free OH groups of the CA, in the GEDTA11 the chains of cellulose acetate are farther apart due to the presence of crosslink and the formation of a three-dimensional network. Thus, the number of repeating units of CA (acetylated cellobiose) is smaller in the GEDTA11. Table 2 shows that the greater the degree of crosslinking, the smaller the percentage of repeating units of CA per cm^3, this explains the higher absorbance of the CA. Because each repeating unit of the CA (DS 2.5) has five acetate groups (esters) and as shown in Fig. 1, one diester is formed during crosslinking of EDTAD and CA. Thus the amount of esters is less per unit volume, which contributed to lower absorbance. Another contribution to the decrease in absorbance at 1932 nm, is the consumption of the OH groups of the AC in the crosslinking esterification.

In 1723 nm (characteristic for CH_2 vibrations) the absorbance was higher in the GEDTA11. Because for each crosslinked EDTAD there are six CH_2 groups, while in each repeating unit of CA there are two CH_2 groups, so higher absorbance in GEDTA11. In 1427 nm (characteristic for combinations of CH and CH_2 vibrations) the large amount of CH groups in the CA contributed to the higher absorbance (Workman, 2000). The pure cellulose was used to investigate overlaps in the spectrum. It was found possible to distinguish structural differences between CA and GEDTA11 by spectra NIR. Through the NIR spectra was possible to obtain additional informations about the structure of hydrogels.

3.5. TG and DTG

Cellulose acetate is degraded in three steps. The first step from the room temperature (25 °C) to 330 °C represents the volatilization of the volatile matter, and/or the evaporation of residual absorbed water. The second step starts at 330 °C and ends at 500 °C, and represents the main thermal degradation of the cellulose acetate chains. The third step starts at 500 °C, and represents the carbonization of the products to ash. The results of thermal degradation of cellulose acetate corroborate results obtained by Hanna (Hanna, Basta, El-Saied, & Abadir, 1999).

After synthesis reactions have formed carboxylic acid groups derived from EDTA-tetra acetic (EDTA acid) in the crosslink. The TG and DTG curves show that the hydrogel is less thermally stable than the CA. This event may be related to the C—N bond present in the crosslinking in the hydrogels. The Fig. 4(E) shows that the C—N bond has lower binding energy, and thus is degraded into lower temperatures.

The thermal stability of EDTA is much lower than AC, thus, the inclusion of EDTAD-grafted and EDTAD-crosslinked in the polymer network makes a proportionate decrease in the thermal stability of the hydrogel. Because the CA presents linear chains which provide a great extent of formation of hydrogen bonds conferring thermal stability of the polymer. The inclusion of crosslink causes the physical separation of the CA chains and consequently the decrease in the intermolecular interactions with a large decrease in the thermal stability of the hydrogel.

3.6. Determination of crosslinking density

The Flory-Rehner theory stems from the combination the Flory-Huggins theory for polymer solvent with the theory of statistical mechanics of the free energy variation caused by swelling. The following equation is related to crosslink density in systems where they move simultaneously and at the same speed ("affine deformation") during the swelling of the sample.

$$\nu = -\left[\frac{ln(1 - V_r) + V_r + \chi V_r^2]}{\rho V_1 (V_r^{1/3} - \frac{V_r}{2})}\right], \quad (5)$$

where: ν = Crosslink density which corresponds to the effective number of chains per unit volume ($\nu = \rho/Mc$) Eq. (6), ρ is the density of the polymer and Mc is average molecular weight between crosslink). V_r = reduced volume (sample volume before swelling/sample volume after swelling). χ = parameter of polymer-solvent interaction. V_1 = molar volume of the pure solvent.

In the method of swelling in the equilibrium, the polymer is immersed in solvents selected with a range of values of solubility parameter. The value of the solubility parameter of the polymer is equal to the solubility parameter of the solvent when the swelling

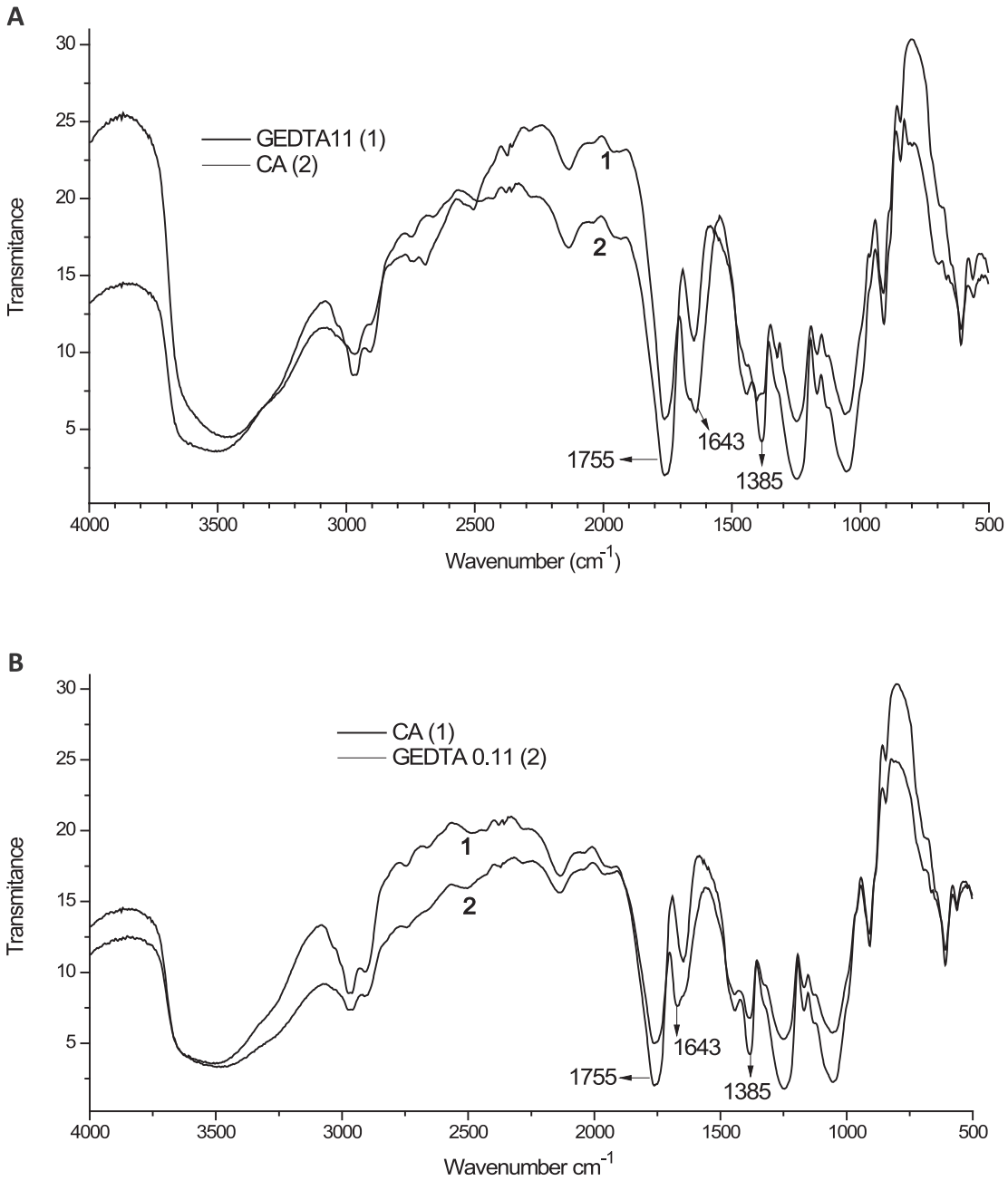


Fig. 2. FTIR spectra of GEDTA11 and cellulose acetate (A) and GEDTA 0.11 and cellulose acetate (B).

is maximized. The degree of swelling in the equilibrium is represented by the parameter Q. The parameter Q is determined experimentally by the relation:

$$Q = \frac{(m - m_0)}{m_0 \times \rho}, \tag{7}$$

where "m_o" is the weight of dry polymer, "m" is the weight of swollen polymer and the solvent density ρ.

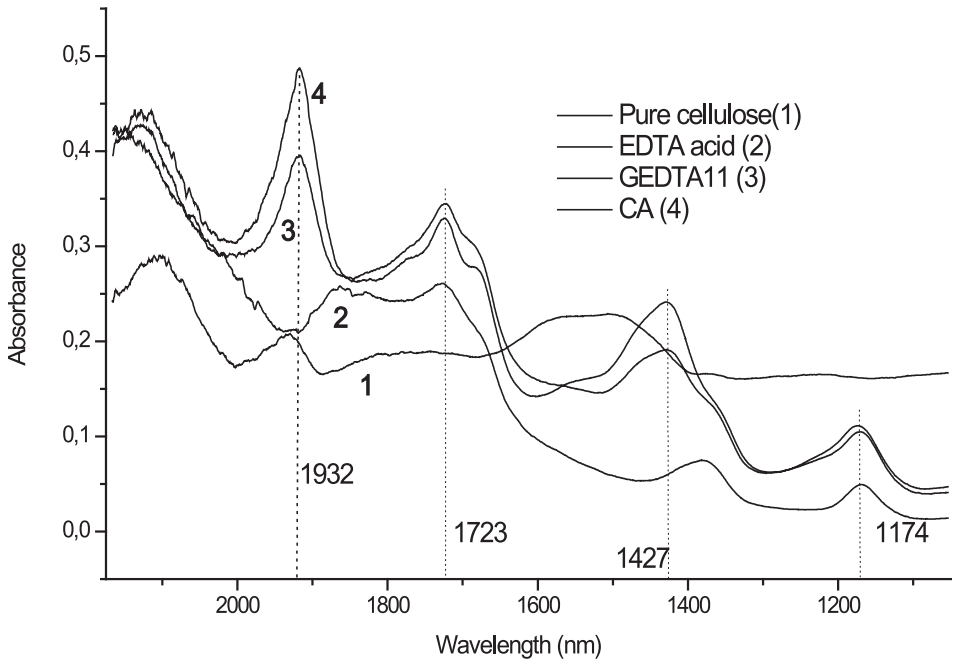
The parameter of interaction polymer-solvent, χ can be decomposed into components of entropy (χs) and enthalpy (χh), as a measure of energy free. Thus:

$$\chi = \chi_s + \chi_h, \tag{8}$$

$$\chi_h = \frac{(\delta 1 - \delta 2)^2}{RT}, \tag{9}$$

where R is the gas constant, T is absolute temperature, $\delta 1$ and $\delta 2$ is the solubility parameter of the solvent and polymer respectively. In conditions of maximum swelling, the contribution of χh is minimal and the value of the interaction parameter is almost equal to the entropy contribution. The literature has used the value of 0.34 for χs (Blanks & Prausnitz, 1964; Dudek & Bueche, 1964). The crosslinking density (ν) and the corresponding average molecular weight between crosslinking points (Mc) were calculated by Eq. (5) and (6).

To investigate the correlation between the percentage of swelling (% S) and Mc was synthesized a hydrogel with crosslink density $\upsilon = 1.19 \times 10^{-6}$, $Mc = 1.1 \times 10^6$, and density 1.308 g/cm^3. This hydrogel was synthesized only to collect the results of swelling in the equilibrium and plot a graph with the results of the hydrogels presented in this work, because this way the investigation of correlation is more statistically significant.

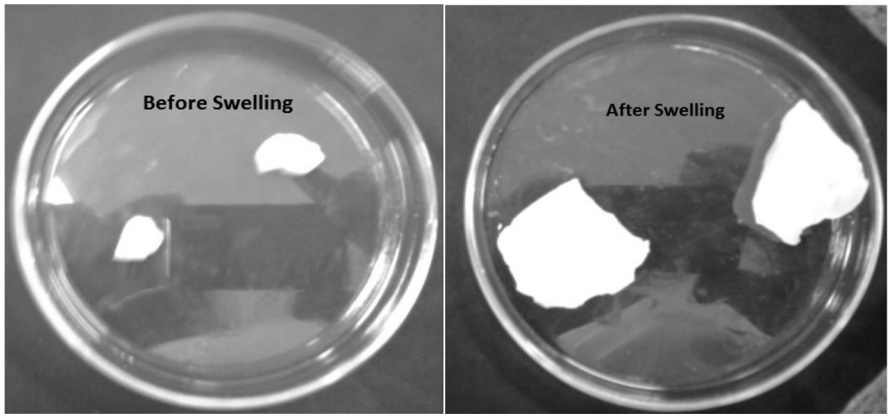


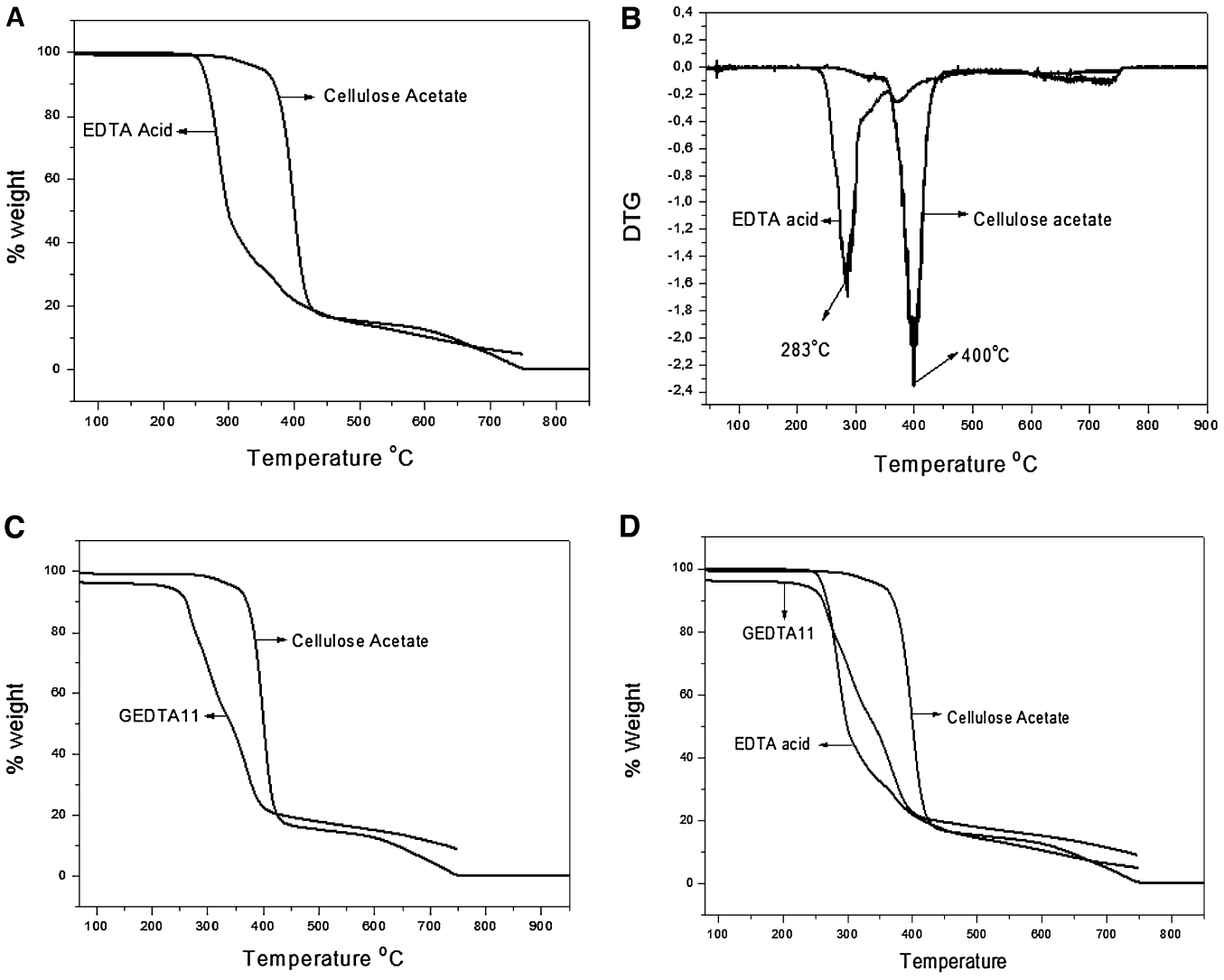
Vibrations (nm)	Description
1932	2nd overtone (Characteristic for ((esters)RCOOR1 and ROH vibrations)
1723	1st overtone (Characteristic for CH_2 vibrations)
1427	1st overtone combinations (CH and CH_2 vibrations)
1174	2nd overtone (CH_3 and CH_2)

Fig. 3. NIR spectra of pure cellulose, CA, EDTA acid, and GEDTA11 in the region 1900–1300 nm.

Table 1
Results obtained by Flory-Rehner theory.

Results of the determination of crosslinking			
Gel	GEDTA11	GEDTA12	GEDTA 0.11
Percentage of absorption in the equilibrium	1142	2450	6800
Maximum swelling in the equilibrium, Q (cm^3/g)	12.1	26.0	72.0
Reduced volume, V_r	0,0581	0,0205	0,0106
Density of gel, ρ (g/cm^3)	1.368	1.332	1.297
Solubility parameter of the gel, $\delta 2$	12.1	12.1	12.1
Interaction parameter polymer-solvent, χ	0.34	0.34	0.34
Density crosslink, (g/cm^3).	1.6×10^{-5}	4.4×10^{-6}	8.2×10^{-7}
Average molecular weight between crosslink, *Mc*	8.2×10^4	3.1×10^5	1.6×10^6
Observation: molar weight of repeat unit 534.5 g/mol			





E

Average Bond Enthalpies (P.W Atkins & L.L. Jones, 1999)

Bond	Average Bond Enthalpies (Kj.mol^{-1})
C-C	348
C-H	412
C-O	360
C-N	305
O-H	463

Fig. 4. TG of cellulose acetate and EDTA acid (A), DTG of cellulose acetate and EDTA acid (B), TG of cellulose acetate and GEDTA11 (C), TG of cellulose acetate, EDTA acid and GEDTA11(D), average bond enthalpies (E).

The hydrogels presented higher swelling in dimethylformamide (Fig. 5A). The Fig. 5B shows that the correlation between S% and *Mc* is very good. Thus, the method used to determine the crosslink density in the hydrogels is accurate.

Fig. 6.

3.7. Determination of total amount of crosslinker agent in the hydrogels

For the elucidation of the structural features of each gel, the number of molecules of EDTA per of repeat unit and the percentages

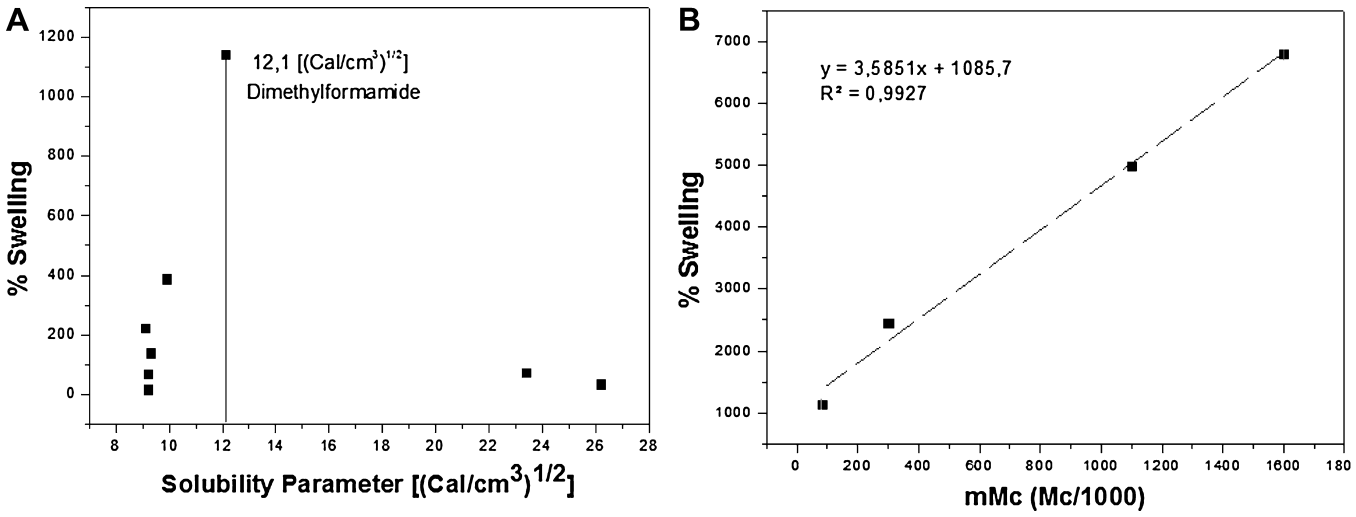


Fig. 5. Valuation of the percentage of swelling (S%) to the hydrogels in different solvents (4A). Correlation between the percentage of swelling (S%) and *Mc* (5B).

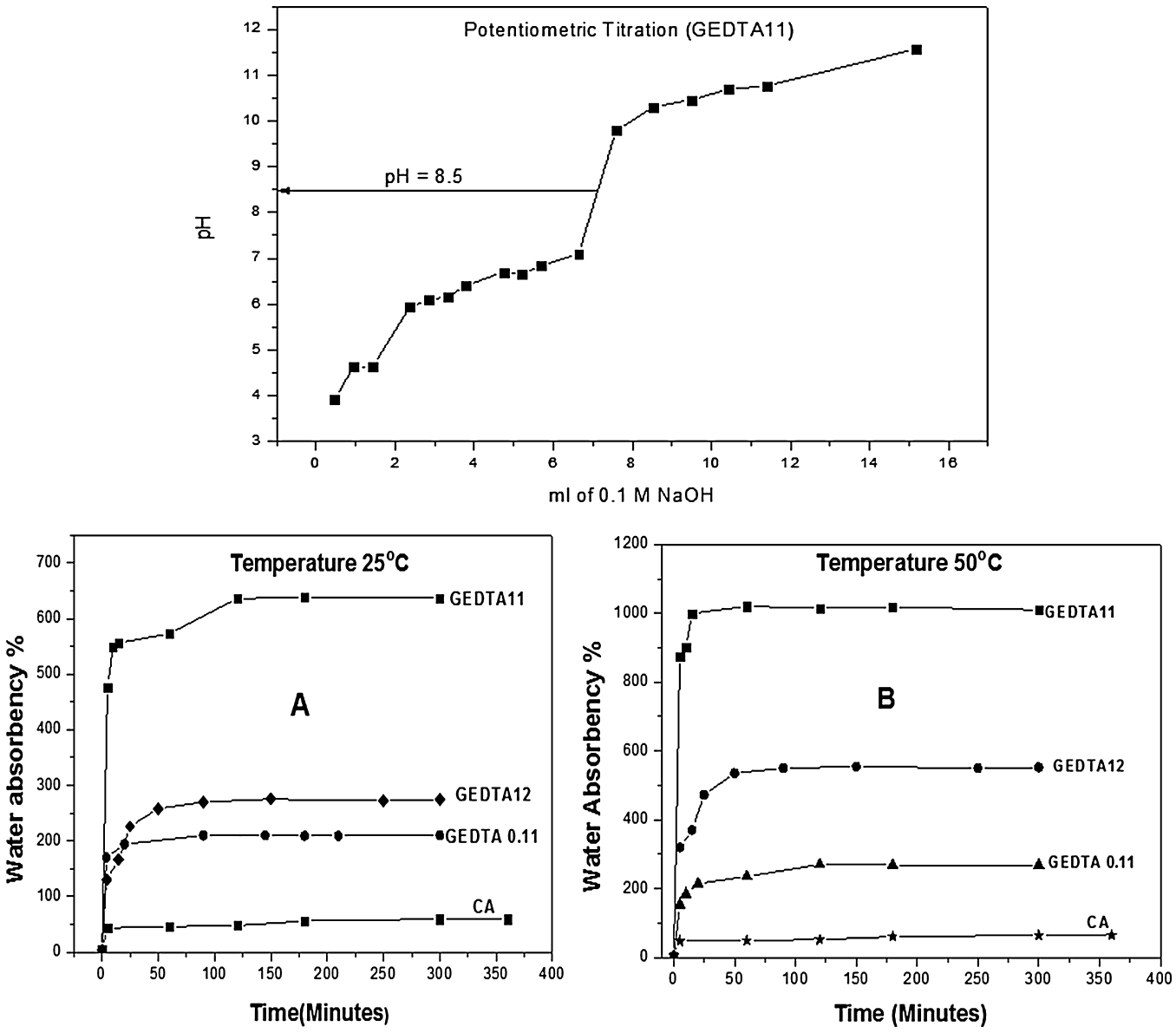


Fig. 6. Water absorbency: Temperature 25 °C Fig. 6A, Temperature 50 °C Fig. 6B and potentiometric titration of GEDTA11.

Table 2
Reaction conditions and results of the esterification crosslinking of cellulose acetate with EDTAD.

Gel	W_{CA} [a]	n_{CA} [b]	% CA [c]	AT_1 (mmol/cm^3) [d]	AT_2 (g/cm^3) [e]	$A._{EDTA}$ [f]	%Cr [g]	%Gr [h]	n_{EDTA} [I]
GEDTA11	1.144	0.0021	83.6	0,7663	0.224	4.61×10^{20}	98.26	1.74	0.36
GEDTA12	1.256	0.0024	94.3	0.2593	0.076	1.56×10^{20}	98.39	1.61	0.11
GEDTA 0.11	1.281	0.0024	98.8	0.0553	0,016	3.3×10^{19}	98.54	1.46	0.02

[a] Grams of CA per cm^3 of gel.
[b] Mol of repeat unit.
[c] Percentage of CA.
[d] mmol of EDTA per cm^3 of gel.
[e] Grams of EDTA per cm^3 of gel.
[f] Number of EDTA molecules per cm^3 of hydrogel.
[g] Percentages of the crosslinked EDTA molecules in total esterified EDTA in each gel.
[h] Percentages of the grafted EDTA molecules in total esterified EDTA in each gel.
[I] Number of EDTA molecules per repeat unit of CA.

of crosslinked-EDTAD and grafted-EDTAD (%Cr and %Gr, respectively) were determined by the titration method for the estimation of the total amount of ester contents. In 1 cm^3 of the hydrogel, it was supposed that there was X mmol of crosslinked EDTAD and Y mmol of grafted EDTAD. As shown in Fig. 1, one diester and two carboxylic acid groups are formed during crosslinking, whereas the graft reaction resulted in the formation of one ester and three carboxylic acid groups. In Comparing the results in Table 2 with results obtained by Kono and Fujita (2012) is possible to conclude that the results of percentage of EDTAD-crosslinked and the percentage of EDTAD-grafted are similar.

To obtain the results shown in Table 2 titration results, and the density of the hydrogels (Table 1) were used. The following equations were used to obtain the results of Table 2.

$$[\mathrm{WCA} = (\rho - \mathrm{AT2})], \tag{10}$$

$$\left[\mathrm{nCA} = \frac{\mathrm{WCA}}{\mathrm{M1RU}}\right], \tag{11}$$

$$\left[\%\mathrm{CA} = \left(\frac{\mathrm{WCA}}{\rho}\right) \times 100\right], \tag{12}$$

$$\left[\mathrm{AT1} = \left(\frac{\mathrm{mmolEDTA}}{\mathrm{SV}}\right)\right], \tag{13}$$

$$\left[\mathrm{AT2} = \left(\frac{\mathrm{weight\,EDTA(g)}}{\mathrm{SV}}\right)\right], \tag{14}$$

M_1RU = molar weight of repeat unit (534.5 g/mol), ρ = density of hydrogel (g/cm^3), SV = sample volume (cm^3).

3.8. Determination of the water absorbency

Potentiometric titration was performed in 1 cm^3 of GEDTA11 with 100 mL of distilled water to find the pH value that all of the carboxylic acid groups are neutralized completely. The value found was 8.5, this value was used as a reference in the neutralization in the hydrogels used in testing water absorbency.

The water absorbency is dependent on the temperature and also the amount of carboxylate groups in the hydrogels. In comparison between hydrogels and CA; was concluded that the hydrogels are more hydrophilic than the CA and thus absorb more water. With the increase of carboxylate groups in the hydrogels, the ionic character along the polymer chain increases. With increasing temperature, increases the diffusion of water into the hydrogel and thus the absorption of water increases.

4. Conclusion

The hydrogels were prepared from cellulose acetate (DS 2.5) via simple esterification crosslinking of EDTAD under mild conditions. Simultaneous crosslinking and grafting of EDTAD occurred by the formation of diester and monoester linkages. The characterizations performed by the techniques of TG and DTG, FTIR and determination of crosslink density proved to be effective in characterization of hydrogels. The hydrogels were produced with raw materials of low cost, through a simple procedure at room temperature and the hydrogels are derived from cellulose, which is a renewable resource.

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