

Influence of degree of substitution on thermal dynamic mechanical and physicochemical properties of cellulose acetate

Roberta R.M. de Freitas, André M. Senna, Vagner R. Botaro*

Universidade Federal de São Carlos-UFSCAR, Rodovia João Leme dos Santos, Km 110, Sorocaba, 18052-780, São Paulo, Brazil

ARTICLE INFO

Keywords:

Cellulose acetate
Degree of substitution
Deacetylation
DMA

ABSTRACT

Deacetylation of commercial cellulose acetate (CA) with initial 2.48 ° of substitution (DS) was studied by alkaline hydrolysis. Kinetic behavior of hydrolysis was studied and samples with different degree of substitutions were obtained as a function of reaction time. Spectrum of deacetylated CA has showed the disappearance of typical band of C=O in 1750 cm^{-1} in comparison to that of CA. Some very important parameters were obtained by techniques employed in samples characterization. For example, water temperature desorption (Td), Glass transition temperature (Tg) and fusion temperature (Tm) were obtained by DSC. Crystallinity index (CI) was obtained by XRD for all samples with different DS values. For comparative purposes, CA sample with DS 2.45 and sample with DS were analyzed by 2.29 DMA. These samples were soluble in acetone and in this way, films with good quality were obtained by casting. This small variation in DS causes significant changes in mechanical property. A decrease in DS of only 0.19 has caused an increase of over 120% in obtained storage modulus at 50 °C with CA DS 2.29.

1. Introduction

Sustainable development has been a concern in recent years. The search for renewable sources materials is increasing year after year in an attempt to replace non-renewable sources (Ghareeb et al., 2012). Beyond the search for materials from renewable sources, there is a great demand for materials that are biodegradable with interesting mechanical properties in general way (Lin and Anseth, 2013). In this sense, cellulose is the most abundant natural polymer in nature, is biodegradable, biocompatible and non-toxic, and comes from clean technologies and renewable sources. Cellulose derivatives study presents great interest (Ghareeb and Radke, 2013; Azzaoui et al., 2015). Cellulose acetate (CA) is the main cellulose derivative, used mostly in membranes, films, fibers, filters, as a component in adhesives and pharmaceuticals (Ghareeb et al., 2012). First reports about the process of cellulose acetylation are assigned by Schutzenberger, at about 1865 (Morgado et al., 2011), and it was produced by replacing the hydroxyl groups present in cellobiose by acetyl groups (Senna et al., 2013). Usually, the cellulose modification is performed with acetic acid and acetic anhydride having sulfuric acid as a catalyst and the degrees of substitution, depending on experimental conditions (Ribeiro et al., 2014).

Cellulose acetate has a great commercial appeal because the material features ease in processing with different solvents and an equally

important way, CA is produced through recycled sources. CA has been used in the hydrogels production to fertilizer controlled-release, showing excellent performance (Senna and Botaro, 2017). In several studies, cellulose acetate has been produced through cellulose from recycled sources, such as bean straw (Brum et al., 2012) and mango seed (DA CRUZ et al., 2011). DS is the average number of acetyl groups replacing the hydroxyl groups per glucose unit. The maximum degree of acetylation is obtained when all OH groups are replaced by acetyl groups, which leads to a DS equal to three. Current literature recognizes that DS greatly affects the mechanical properties and CA solubility (Casarano et al., 2011). The replacement of cellulose OH groups by acetyl groups makes the polymer more soluble, with different thermal, chemical, physical and mechanical properties (Samios et al., 1997). DS increases lead to polymer more soluble in solvents such as THF and acetone. Known, cellulose (DS = 0) is insoluble in most traditional solvents (Kono et al., 2015). Cellulose diacetate is soluble in acetone or tetrahydrofuran (THF), while cellulose triacetate is soluble in dichloromethane and other chlorinated solvents (Ghareeb and Radke, 2013).

Deactivation reaction is inversion of acceptance reaction, where acetyl groups are replaced by OH in alkaline hydrolysis (Ghareeb and Radke, 2013). The DS determination is essential because this parameter can affect chemical, physical, mechanical and morphology cellulose acetate characteristics (Ghareeb and Radke, 2013). The literature does

* Corresponding author.

E-mail address: vagner@ufscar.br (V.R. Botaro).

<http://dx.doi.org/10.1016/j.indcrop.2017.08.062>

Received 14 March 2017; Received in revised form 29 June 2017; Accepted 31 August 2017
Available online 25 September 2017

0926-6690/© 2017 Elsevier B.V. All rights reserved.

not present many comparative data between different ways to generate deacetylation reactions. Still, few works point out thermal dynamic mechanical studies of cellulose acetates in DS function. This work evaluated cellulose deacetylation of acetate and samples were characterized with different degrees of substitution using the DMA, DSC, XRD, FTIR and SEM analyses. Very small variations in the degree of substitution caused significant changes in the polymers mechanical property.

In general, there are few works that relate degree of substitution of thermoplastic polymers and mechanical, thermal and structural properties. According to our search in the literature, authors believe that there are not detailed studies involving dynamic mechanical properties of cellulose acetate based on the degree of substitution.

2. Materials and methods

2.1. Materials

Pellets cellulose acetate was provided by the RhodiaSovay[®] group. Typically, the polymer features degree of substitution equal 2.48. Other solvents and reagents are commercial and with over 99% purity, as acetone and sodium hydroxide. Pure cellulose sample, obtained from the Whatman 1 paper filter, was used for comparative purposes, as a sample with DS = 0.

2.2. Methods

2.2.1. Deacetylation of cellulose acetate

15 g of CA (DS 2.48) were added into beaker containing 300 ml of water and 315 ml of NaOH 0.5 M at 20 °C ± 0.5 under constant stirring. In 10, 15, 25, 60, 90, 120, 180, 240 and 330 min, samples of approximately 1.0 g were collected for future analysis.

2.2.2. DS determination

CA was placed in an oven for 1 h at 80 °C and after in a desiccator at room temperature. A solution of c.a 0.500 g of CA and 20 ml ethanol/water solution 75% v/v was prepared using an erlenmeyer flask. The system was covered and heated for 30 min at 60 °C in water bath, and then a solution of 25 ml of NaOH 0.5 M was added to mixture. The reaction medium was heated for 15 min at 60 °C and after for 72 h at room temperature. The excess of NaOH was titrated with standardized HCl solution 0.5 M. The same procedure described above was conducted using c.a. 0.500 g of filter Whatman paper finely divided and dry in an oven. The DS was calculated according to Standard Test Methods for Cellulose Acetate ASTM D 871-96 (ASTM, 2004):

$$\%Acetyl = \frac{\{(V_{NaOH} \times A) - (V_{HCl} \times B) - [(V'_{NaOH} \times A) - (V'_{HCl} \times B)]\}}{w} \times 4.3 \quad (1)$$

$$DS = \frac{3.86 \times (\%Acetyl)}{102.4 \times (\%Acetyl)} \quad (2)$$

% Acetyl is the percentage of acetyl groups in the sample; A is the concentration of the NaOH solution in mol/L; B is the concentration of the HCl solution in mol/L; V_{NaOH} and V'_{NaOH} are the volumes (L) of the NaOH solution added in the samples and in blank, respectively; V_{HCl} and V'_{HCl} are the volumes (L) of HCl added in the samples and in the blank and w is the mass of the sample in grams.

2.2.3. FTIR analysis

CA samples with known DS were analyzed by FTIR in order to verify the appearance or disappearance of specific bands during the deacetylation process. FTIR pellets were prepared by using mixtures of CA samples and KBr and typical parameters include 32 scans in the range of 500–4000 cm⁻¹.

2.2.4. DSC analysis

The differential scanning calorimeter was used to examine the thermal property of the CA samples in a temperature range of 25–300 °C. Approximately 10 mg of the CA samples with DS 2.48, 2.29, 1.98 and 1.48 were used. The measurements were performed in a pan Al, pierced lid in the N₂ atmosphere (flow rate of 50 ml/min) at a heating rate of 5 °C/min. The results were recorded and analyzed.

2.2.5. XRD analysis

A diffractometer was used with a goniometer speed of 2/min, in the range of 7–70° (2θ) iron pipe. Ruland-Vonk methodology (Karimi and Taherzadeh, 2016) was the base for determination of crystallinity index (CI):

$$CI = \left(\frac{Sc}{St} \right) \times 100 \quad (3)$$

Where Sc is the area of the crystalline domain and St is the total area.

2.2.6. Characterization by dynamic-mechanical thermal analysis: DMA

CA films were prepared by casting. The samples used for preparation of the films were commercial sample with DS 2.48 and CA sample with DS 2.29. Sample with DS 2.29 was obtained by deacetylation of the commercial sample. These samples were chosen because both have showed great solubility in the process of films preparation. Casting solutions: Samples were prepared by using a typical concentration of 2% (m/v) CA in tetrahydrofuran. After solubilization, the samples were added in the Petri dish that it was covered at room temperature for about four days. A model Q 800 TA Instruments with tension film claw was used in order to obtain E'; E'' and tan delta values. The films had approximate dimensions 10/7/0.5 mm, length/width/thickness respectively. Frequency of 1 Hz, preload 0.15N, 4000 μm of amplitude, and a ratio of 3 °C.min-1 of heating and a range of 40–270 °C were typical for DMA analysis.

2.2.7. SEM analysis

The cellulose acetates were kept in an oven with a temperature of 60 °C for approximately 24 h in order to reduce the humidity. The surfaces of the samples were analyzed in a SEM model TM 3000 Hitachi with 5 Kv acceleration and wit 800 times magnification.

3. Results and discussion

3.1. Cellulose acetate deacetylation

The deacetylation processes is a simple and interesting methodology for obtaining CA samples with different DS. The kinetic of the reaction was studied and the samples obtained with different DS were characterized based on morphology and thermal behavior. Table 1 shows DS with the reaction time for experiments in heterogeneous medium.

Table 1 shows that the DS values decrease gradually during the course of hydrolysis. It may be noted that the process is slow and a

Table 1
DS with the reaction time for experiments in heterogeneous medium.

Time/min	DS
0	2.48 ± 0.04
10	2.42 ± 0.07
25	2.29 ± 0.01
60	1.98 ± 0.01
90	1.48 ± 0.05
120	1.23 ± 0.09
180	0.76 ± 0.08
240	0.65 ± 0.14
330	0.38 ± 0.07

relatively long time is required to obtain a CA with low DS. CA deacetylation with DS 2.48 by homogeneous hydrolysis with acetic acid as solvent and sulfuric acid as a catalyst was published previously. Samios et al. (1997) have pointed out that kinetic of deacetylation reaction is far superior when the environment is homogeneous. In homogeneous environment, polymeric chains are in solution and have greater mobility. In this way, effective shocks are very frequent and the speed of reaction is greater. The authors have showed that the homogeneous hydrolysis is more effective in the first moments of reaction and smaller DS values were obtained when compared to Table 1. Just as an example, the authors obtained a sample of CA with DS 1.7 after 25 min of reaction in a homogeneous deacetylation process. Table 1 shows a much higher value for the DS (2.29) for heterogeneous phase reaction in the same time interval

3.2. Kinetic studies of the reaction

Kinetic study based on integral analysis is an interesting model for the deacetylation reaction in heterogeneous environment. The objective was to determine the reaction order. The knowledge of reaction order is important since kinetic laws help to develop mechanisms of reaction, formation and breaking of bonds that occur during the conversion of the reagents into products. (Kotz et al., 2006). Fig. 2 shows the processing of data considering the kinetic equation of first order (Eq. (2)):

$$\ln(C_t) = \ln(C_0) - Kt \quad (4)$$

Where C_t representing concentration of acetyl group during de reaction time; C_0 is the concentration at initial time; K is the Kinetic constant and t is time.

Fig. 1 shows an excellent correlation with R^2 around the 0.99, which can be regarded as a near-perfect line. This fact indicates strongly that the CA deacetylation follows a kinetic reaction of first order. The occurrence of reaction kinetic of first order was expected since one of the reagents is insoluble in the reaction medium.

3.3. FTIR analysis

FTIR is a great technique to analyze modification reactions generally. Specifically for the deacetylation process, typical carbonyl stretching band of acetate group is very intense and can be easily quantified. These carbonyl bands of acetyl groups are very visible and appear in an isolated region of FTIR spectrum at 1750 cm^{-1} . Fig. 2 shows the spectrum of cellulose, CA with DS 2.48 and deacetylated CA with DS 0.08 obtained by hydrolysis. As expected, typical bands found after an intense hydrolysis is practically the same of cellulose. Fig. 2 shows the FTIR spectra for a sample of cellulose, commercial CA with DS 2.48 and deacetylated CA sample with DS 0.76. It is notorious disappearance of typical carbonyl band at 1750 cm^{-1} after deacetylation when acetyl groups are replaced by hydroxyl ones. The asymmetric stretching band of CH_3 (acetyl) also shows the success of deacetylation. This band is very intense at 2920 cm^{-1} in FTIR spectrum of commercial

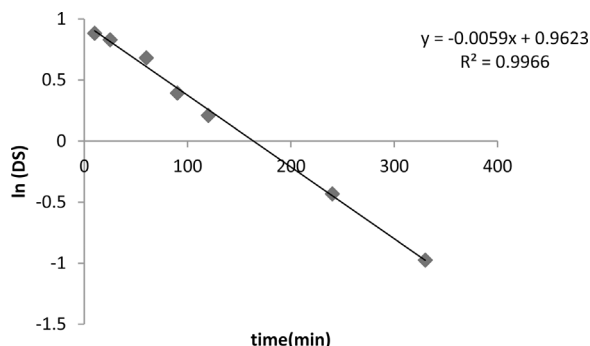


Fig. 1. First order kinetic model applied to deacetylation in heterogeneous medium.

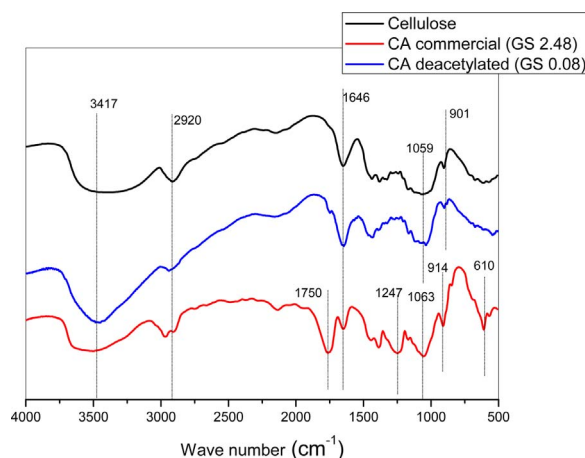


Fig. 2. FTIR spectrum: commercial CA, CA with DS 0.08 and cellulose.

CA and non-existent in the CA sample with DS equal to 0.08.

Equally important is the disappearance of C–O stretching band of acetate groups that is very visible in the spectrum of CA at 1247 cm^{-1} and absent after hydrolysis. Significant differences are also observed at 610 cm^{-1} related to presence of stretching band of C-acetyl groups. As also expected, this band is very visible in the spectrum of commercial sample, absent in cellulose and deacetylated CA (Silverstein et al., 2005).

The samples obtained by heterogeneous hydrolysis were also analyzed by FTIR. Fig. 3a shows the spectra obtained for cellulose, commercial CA sample and deacetylated samples while Fig. 3b highlights the carbonyl groups of acetate at 1750 cm^{-1} . Some modifications are important as, for example, the increased intensity of stretch bands OH (3450 cm^{-1}) due to the decrease in the degree of acetylation. It can also be observed an increase in the typical band stretching of acetyl group (CH_3) in function of increase of the DS (Fig. 3a). Fig. 3b clearly shows a decrease in the carbonyl stretching band due to the decrease in the DS.

3.4. Characterization by X-ray diffraction: XRD

The characterization by X-Ray Diffraction (XRD) was performed to evaluate change in crystallinity and the morphological alterations of the cellulose acetates with different DS. Fig. 4 presents the results of cellulose acetates with DS 2.48, 2.29, 1.98 and 1.48.

XRD show typical patterns are semi-crystalline materials with amorphous and crystalline phases. The results feature a wide halo around the $2\theta = 20^\circ$ known as van der Waals or amorphous and this halo is normally found in all organic polymers. Can also be noticed a maximum around $2\theta = 10^\circ$, known as low van der Waals halo (Wan Daud and Djuned, 2015). In the literature, this maximum is corresponding to the existence of regions with aggregates of parallel chains segments. Another important peak and characteristic of semi crystallinity is located next to $2\theta = 8^\circ$. This peak indicates the disorder when cellulose is acetylated. With acetylation, acetyl groups cause an increase in the interfibrillar distance and break of microfibrillar structure. The position of the peak indicates the generation of a disorder and shows that cellulose is acetylated (Wan Daud and Djuned, 2015). CA with the lowest DS features a decrease of this peak intensity. It is important note that with the decrease in DS, the amorphous halo near $2\theta = 20^\circ$ has its intensity reduced.

According to Chen et al. (2016) the crystalline cellulose acetate diffractions are marked by narrower peaks, in approximately $2\theta = 8^\circ$, 10° and 13° . Fig. 4 shows that the commercial CA sample with DS 2.5 presents only a very low profile in halo $2\theta = 13^\circ$. The increase in hydrolysis makes the halo in $2\theta = 13^\circ$ more acute and visible to all samples. Polymer chains are approximated with the replacement of the acetyl groups for hydroxyl ones. In this way, the interaction between

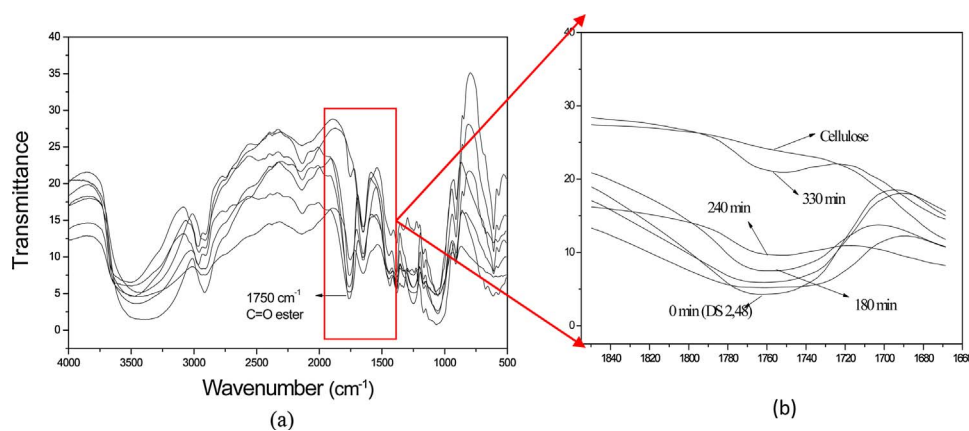


Fig. 3. (a) FTIR spectra of samples of CA for different hydrolysis times with (b) expansion of the 1750 cm^{-1} bands related to vibrations of stretching of carbonyl ($\text{C}=\text{O}$).

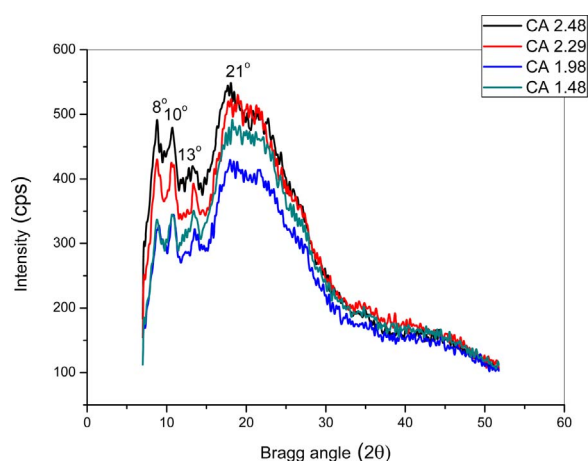


Fig. 4. XRD of cellulose acetates with DS 2.48, 2.29, 1.98 and 1.48.

the polymer chains by the formation of hydrogen bonds increases and consequently the organization of chains and the percentage of crystalline phase are higher after hydrolysis.

The analyses of XRD have complex data analysis. There are three main methods for determination of crystallinity index (CI) of a polymer based on the results of XRD (Karimi and Taherzadeh, 2016). The method used which consists of calculating by dividing the peak height (200) (the maximum interference; I_{200}) and the minimum height between the peaks (200) and (100) (intensity the $2\theta = 18^\circ$). However, this method is more usual for determination of CI of cellulose. Another method is known as deconvolution, curve adjustment, the peak for crystalline and amorphous region parts, and used Gaussian, Lorentzian functions, and Voigt. The difficulty of this method is to select the appropriate peaks, and some authors use various hypotheses for determination of CI. The third method is known as amorphous or subtraction Ruland-Vonk, this method is based on the relationship between the area of crystalline domains by the total area, as shown in Eq. (1) (Karimi and Taherzadeh, 2016). Determination of CI was done by Ruland – Vonk method (Eq. (1)). The values of CI for the DS samples 2.48, 2.29, 1.98 and 1.48 were respectively 23%, 30%, 31% and 34%. This increase in crystallinity is explained by the replacement of the acetyl groups by hydroxyl groups that have smaller volume than the acetyl. This leads to greater organization of the chains, increasing the intermolecular interactions via hydrogen bonding and increasing crystallinity.

3.5. Characterization by differential scanning calorimetry: DSC

The desorption phenomena; glass transition temperature and melting temperature were evaluated by DSC. Fig. 5 shows the curves by

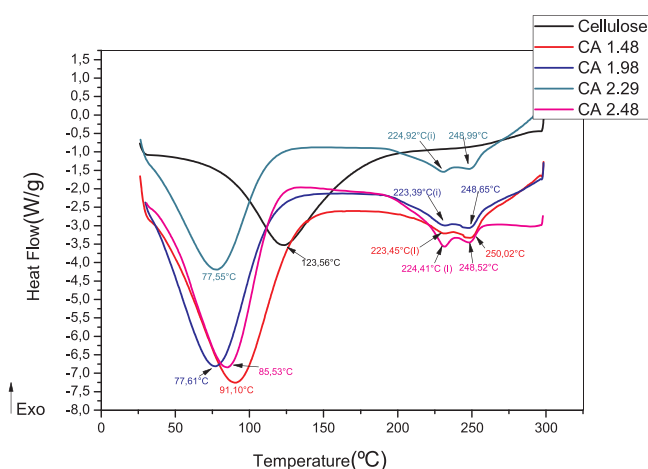


Fig. 5. Curves of DSC to cellulose and CA with different DS.

DSC of cellulose and cellulose acetate samples with different degrees of substitution.

The first endothermic event visible to all samples corresponds to desorption of water. This event occurs at different temperatures depending on the degree of substitution of the sample. This event may vary between 77.5 and 91.1°C approximately as show in Fig. 5. Desorption occurs due to presence of residual moisture or low boiling point solvents. The variance of the values of desorption peak in polymers is explained by the different water-holding capabilities and polymer-water interaction. The data show that samples with lower DS has higher values of desorption temperature. Water molecules interact strongly with hydroxyl groups present in the CA chain through hydrogen bonds. These interactions can be extremely intensive in the case of pure cellulose. However, after acetylation, OH groups are replaced by acetate groups and visible water content is observed (Wan Daud and Djuned, 2015). It is very important to note that cellulose presented only an endothermic event quite evidenced in 123.5°C approximately. Cellulose is a physical thermosetting polymer shows no T_m .

The second endothermic peak on the graph corresponds to the glass transition temperature, which was identified as the average temperature. Known, DSC method is not a precise method for the determination of T_g compared to DMA where the T_g is determined by the maximum Tan Delta peak. T_g results obtained show that the degree of acetylation not modified glass transition temperatures in a significant way. On the other hand, the results obtained from the start of the event and final show differences. This fact is evident when compared to cellulose samples and sample CA commercial with DS 1.98. The event of T_g noted for cellulose starts in 221°C while for commercial CA is 6°C minor. Again, the acetyl groups decrease the intensity of the formation of hydrogen bonds and lower temperatures are needed for the

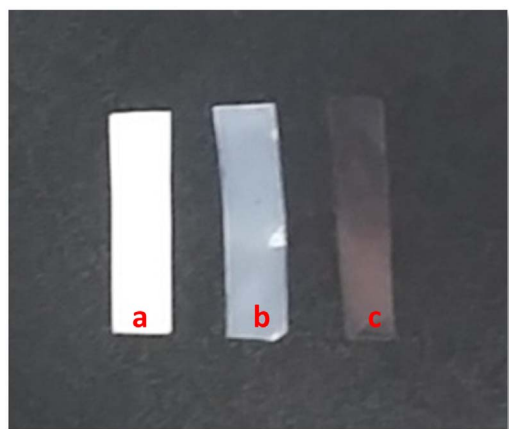


Fig. 6. Cellulose (A), AC 2.29(B) and AC 2.48 film (C).

beginning of event of the Tg.

The melting temperatures of the CA samples were very close, between 248 and 250 °C. The enthalpies of fusion were calculated between 0.9 and 2.4 J/g. According to the literature, values of this order of magnitude are typical of samples with low crystallinity (Kendouli et al., 2014). The results of the analysis of XRD corroborate with that information, because it has been found that the acetates with higher DS has lower crystallinity indices.

3.6. Dynamic mechanical thermal analysis: DMA

Fig. 6 shows images of cellulose paper and CA films with DS 2.29 and 2.48. Acetylation modifies crystal structure of cellulose and results of the XRD have showed the decrease of CI with increase in DS. The presence of acetyl groups in the sample CA 2.29 partially prevents the packaging process of cellulose chains and polymer becomes more amorphous and less opaque (Fig. 6b). Similarly, the increase in the degree of modification results in a more amorphous, transparent polymer, as seen clearly by CA 2.48 (Fig. 6c).

Fig. 7a shows the storage module (E') with the temperature variation for the commercial CA and CA 2.29. In a manner well known in literature, E' module increases with the degree of crystallinity of polymers in general (Callister and Rethwisch, 2012). In an opposite way, E'' decreases with increasing crystallinity. Sample with a lower degree of acetylation has presented a greater storage module E' for the entire temperature range (Fig. 7a). Just as an example, comparative to the temperature of 50 °C, E' for CA 2.29 was about 120% higher than the value obtained by the commercial sample. During the process of deacetylation, acetyl is replaced for hydroxyl ones, and this fact provides a better packaging of the chains promoted by hydrogen bonding, which is reflected in a more rigid, crystalline material. An important factor to note is that a small change in DS (only 0.19) can significantly change the mechanical behavior of the material as a function of temperature.

While commercial sample has no resistance at temperatures close to 180 °C (E' around zero), CA 2.29 presents a rather significant module at this temperature, with value close to 200 MPa. Considering commercial applications of cellulose acetates, this information is extremely relevant, since the CA with DS 2.29 still has excellent processing conditions and higher resistance to Commercial CA in all analyzed temperature range.

Fig. 7b presents the loss module as temperature function for commercial and CA 2.29. CA 2.29 has presented less secondary relaxations (two) than the CA 2.48 (three). This may be explained because the CA 2.48 possess more side acetyl groups than AC 2.29 that has more OH groups.

The maximum peak temperature of tan delta is set to glass transition temperature in DMA tests (Fig. 7c). Hydrogen linkages hamper the

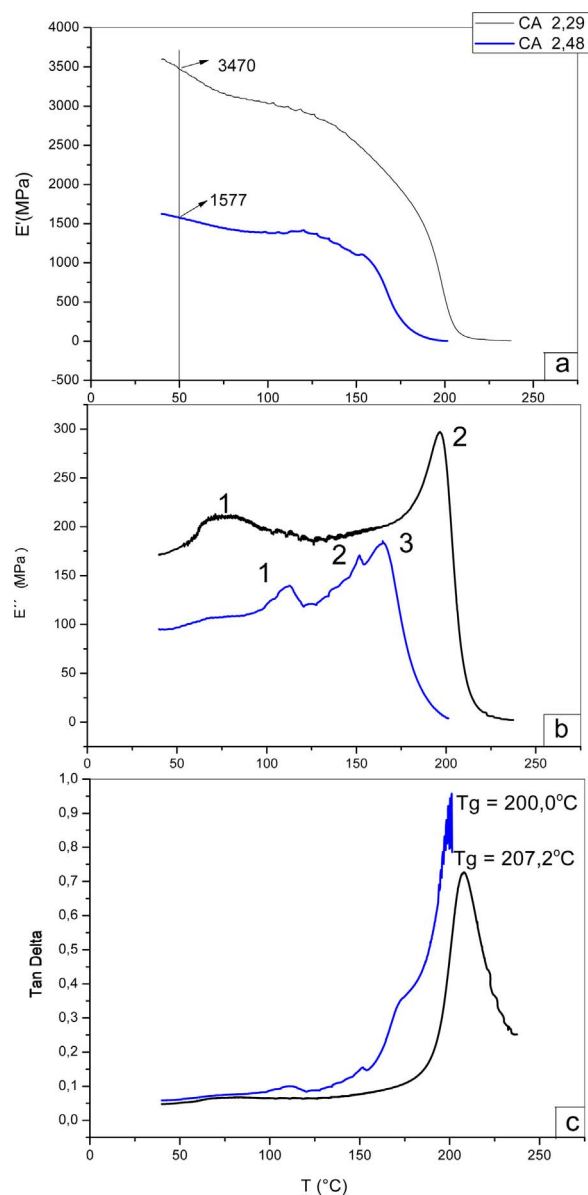


Fig. 7. DMA results to AC2.48 and AC2.29: (a) E' (b) E'' (c) Tan delta in the range of temperature analysis.

mobility of the chains in the region of glass transition temperature. As expected, Tg of CA 2.29 was higher (207.2 °C) as a function of the existence of a greater extent of hydrogen bonds than in the commercial sample.

Tg results obtained in our study are very close to those reported in the literature using the same technique. In other works, found in the literature, the Tg of the CA 2.48 is found near to 200 °C (Gutiérrez et al., 2014).

3.7. SEM analysis

According to Krishnamachari et al. (2011), SEM is a very interesting technique to study the diverse morphology of cellulose. The mechanical, physical, and environmental properties of cellulose depend on the Molecular, supramolecular and morphological cellulose structure. Authors have shown an interesting review involving fibrillar characteristics of cellulose.

Fig. 8 shows the results of SEM obtained for CA and samples with different DS values. MEV analysis were important to evaluate the difference in morphology of the CA samples depending on the DS.

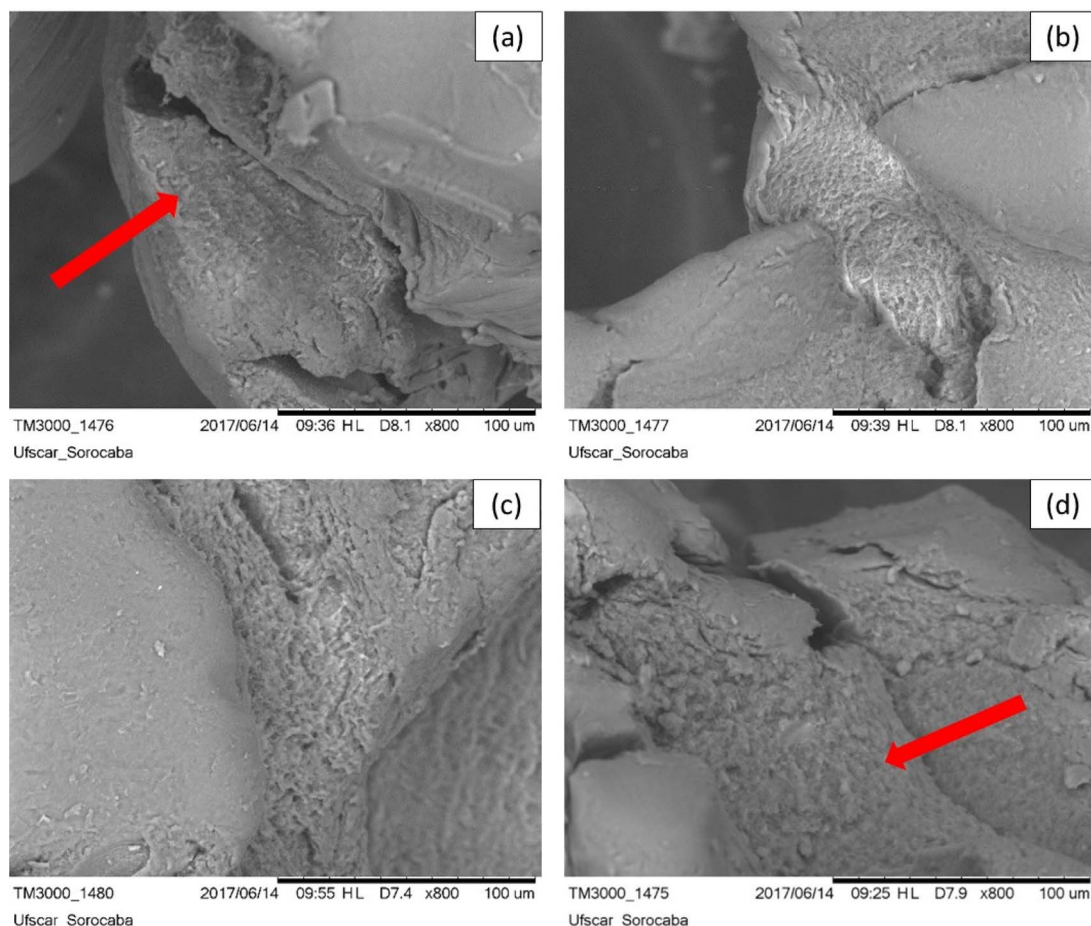


Fig. 8. SEM images of samples of CA: (a) 1.48 DS (b) 1.98 DS, (c) 2.29 DS and (d) DS 2.48 Magnification 800X.

In general, decreased acetylation leads to samples present greater organization of fibrils. For example, in Fig. 8 (a) can be observed a fibrillar organization indicated by the red arrow. On the other hand, samples with higher DS feature less surface fibrillating, with tendency to the formation of spongy type surfaces with shown by the arrow in Fig. 8(d). Samples with lower DS have structures more similar to those of cellulose.

As was proven by x-ray analyses, DSC and DMA, samples with lower DS feature crystalline structures. Therefore, cellulose chains with fewer acetyl groups have better packaging and thus better organized and crystalline structures. Acetyl groups bulky hinder organization of chains that become more disorganized and amorphous.

4. Conclusions

Cellulose acetate with different degrees of substitution were prepared by heterogeneous alkaline hydrolysis. An important factor to note is that a small change in DS (only 0.19) can significantly change the mechanical behavior of the material as a temperature function. Considering the results obtained by DMA, it can be pointed out that CA 2.29 presents advantages over commercial CA when are reviewed elastic modules (E') in wide range of temperature. Additionally, CA 2.29 can be processed with only 7 °C higher than the commercial product, which does not cause significant changes in processing energy.

Acknowledgements

JP Project 2008-00835 FAPESP, CNPq and Capes

References

- American Society for Testing and Materials -ASTM, 2004. ASTM D 871-96: Standard Tests for Cellulose Acetate. ASTM.
- Azzaoui, K., Mejdoubi, E., Lamhamdi, A., Zaoui, S., Berrabah, M., Elidrissi, A., Hammouti, B., Fouda, M.M.G., Al-Deyab, S.S., 2015. Structure and properties of hydroxyapatite/hydroxyethyl cellulose acetate composite films. *Carbohydr. Polym.* 115, 170–176.
- Brum, S.S., Oliveira, L.C.A., de Bianchi, M.L., Guerreiro, M.C., Oliveira, L.K., de Carvalho, K.T.G., 2012. Synthesis of cellulose acetate from the bean straw using *N*-bromo-succinimide (NBS) as catalyst. *Polímeros* 22 447–445.
- Rethwisch Jr., W.D., Rethwisch, D.G., 2012. *Materials Science and Engineering: An Introduction*, 8th ed. John Wiley & Sons, Inc, United States of America.
- Casarano, R., Fidale, L.C., Lucheti, C.M., Heinze, T., Seoud, O.A.E., 2011. Expedient, accurate methods for the determination of the degree of substitution of cellulose carboxylic esters: application of UV-vis spectroscopy (dye solvatochromism) and FTIR. *Carbohydr. Polym.* 83, 1285–1292.
- Chen, J., Xu, J., Wang, K., Cao, X., Sun, R., 2016. Cellulose acetate fibers prepared from different raw materials with rapid synthesis method. *Carbohydr. Polym.* 137, 685–692.
- Cruz, A.C., Meireles, C.S., Ribeiro, S.D., Rodrigues Filho, G., Assunção, R.M.N., de Cerqueira, D.A., Zeni, M., Poletto, P., 2011. Utilization of cellulose acetate produced from mango seed cellulose as matrix for production of microparticles systems. *Quím. Nova* 34, 385–389.
- Ghareeb, H.O., Radke, W., 2013. Characterization of cellulose acetates according to DS and molar mass using two-dimensional chromatography. *Carbohydr. Polym.* 98, 1430–1437.
- Ghareeb, H.O., Malz, F., Kilz, P., Radke, W., 2012. Molar mass characterization of cellulose acetates over a wide range of high DS by size exclusion chromatography with multi-angle laser light scattering detection. *Carbohydr. Polym.* 88, 96–102.
- Gutiérrez, M.C., De Paoli, M.-A., Felisberti, M.I., 2014. Cellulose acetate and short curauá fibers biocomposites prepared by large scale processing: reinforcing and thermal insulating properties. *Ind. Crops Prod.* 52, 363–372.
- Karimi, K., Taherzadeh, M.J., 2016. A critical review of analytical methods in pretreatment of lignocelluloses Composition, imaging, and crystallinity. *Bioresour. Technol.* 200, 1008–1018.
- Kendouli, S., khalfallah, O., Sobti, N., Bensouissi, A., Avci, A., Eskizeybek, V., Achour, S., 2014. Modification of cellulose acetate nanofibers with PVP/Ag addition. *Materials Science in Semiconductor Processing. Int. Semicond. Sci. Technol. Conf. ISSTC-2014*

- 28, 13–19.
- Kono, H., Hashimoto, H., Shimizu, Y., 2015. NMR characterization of cellulose acetate. Chemical shift assignments, substituent effects, and chemical shift additivity. *Carbohydr. Polym.* 118, 91–100.
- Kotz, J.C., Treichel, P.M., Weaver, G.C., 2006. *Chemistry & Chemical Reactivity*, 6th ed. Thomson Brooks/Cole, Belmont.
- Krishnamachari, P., Hashaikeh, R., Tiner, M., 2011. Modified cellulose morphologies and its composites; SEM and TEM analysis. *Micron* 42, 751–761.
- Lin, C.-C., Anseth, K.S., 2013. Chapter II.4.3 – the biodegradation of biodegradable polymeric biomaterials. In: Lemons, B.D.R.S.H.J.S.E. (Ed.), *Biomaterials Science*, 3rd ed. Academic Press, pp. 716–728.
- Morgado, D.L., Martins, V. da C.A., Plepis, A.M. de G., Frollini, E., 2011. Aggregation of chains of cellulose acetates in LiCl/DMAc: evaluation via viscometry. *Polímeros* 21, 143–145.
- Ribeiro, E.A.M., Rodrigues Filho, G., Vieira, J.G., Sousa, R.M.F., de Assunção, R.M.N., de Meireles, C.S., Duarte, J., Zeni, M., 2014. Characterization of asymmetric membranes of cellulose acetate from recycling of residue corn stover for use in ultrafiltration. *Quím. Nova* 37, 385–391.
- Samios, E., Dart, R.K., Dawkins, J.V., 1997. Preparation, characterization and biodegradation studies on cellulose acetates with varying degrees of substitution. *Polymer* 38, 3045–3054.
- Senna, A.M., Botaro, V.R., 2017. Biodegradable hydrogel derived from cellulose acetate and EDTA as a reduction substrate of leaching NPK compound fertilizer and water retention in soil. *J. Controll. Release* 260, 194–201.
- Senna, A.M., Menezes, A.J., de Botaro, V.R., 2013. Study of the crosslinking density in superabsorbent gels obtained from cellulose acetate. *Polimeros* 23, 59–64.
- Silverstein, R.M., Bassler, G.C., Morrill, T.C., 2005. *Carboxylic acid and amines. Spectrom. Identif. Org. Comp.* 7, 96–102.
- Wan Daud, W.R., Djuned, F.M., 2015. Cellulose acetate from oil palm empty fruit bunch via a one step heterogeneous acetylation. *Carbohydr. Polym.* 132, 252–260.