Insights Into Activation of Dissolving Pulp Preceding Cellulose Acetylation

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The current study was conducted to identify the most important variables in the activation phase of cellulose acetate production. Dry alpha cellulose pulp as raw material was supplied by a local company with the intrinsic properties of viscosity equal to 926 mL/g and a water content of 96%. In this regard, the activation phase variables, including reaction time (T30, T60, and T90 min), the addition level of acetic acid (C25, C35, and C45 units per 100 units of dry cellulose), and sulfuric acid catalyst (H0, H0.1, H0.5, and H1%), were experimented followed by characterization of the activated pulp properties through water retention value (WRV), carboxyl groups, viscosity, reactivity, and Fourier transform infrared (FTIR) spectroscopy analysis of fibers. The results indicated that cellulose activation is a complex process with an inverse or contributing effect of the variables. The data were extensively discussed considering the swelling effects governed by diffusion and chemical reactions in both crystalline and amorphous regions of fibers. Eventually, those findings conveyed that the activation process with the above-mentioned conditions was able to improve the properties of cellulose for acetylation phase particularly by increasing reaction time in acid acetic and H_2SO_4 catalyst consumption.

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INTRODUCTION

Cellulose acetate (CA) is one of the most important commercial cellulose derivatives. It is used in various applications, such as textiles, tobacco manufacturing, and production of filter membranes for separation processes, such as gas separation, dialysis, drug delivery, and reverse osmosis (Senna *et al.* 2014; Araújo *et al.* 2020; Homem and Amorim 2020; Wsoo *et al.* 2020).

Large-scale industrial development of cellulose esters of organic acids dates back to the 1920s (Fordyce 1945). Generally, cellulose acetate is produced from dissolving pulp or so-called chemical cellulose with high alpha cellulose content (usually above 95%) (Agreda 1993). Currently the main raw material (dissolving pulp) for the production of cellulose acetate is produced from wood pulp and cotton linter (Homem and Amorim 2020), though many alternative resources have been cited in the literature, such as bamboo (He *et al.* 2009), sugarcane bagasse (Candido *et al.* 2017), *Posidonia oceanica* as a renewable marine biomass waste (Coletti *et al.* 2013), rice straw (Ebrahim *et al.* 2016), newspaper, and mango seed (Meireles *et al.* 2010). The best processes to produce the dissolving pulp from wood are pre-hydrolysis assisted by kraft and acidic sulfite pulping, due to their ability to hydrolyze most of the hemicelluloses in the raw material. Because lignin and hemicelluloses are removed during the production of dissolving pulp, the efficiency of conversion is effectively increased during the synthesis of cellulose derivatives (Saka 2004a,b; Saka and Matsumura 2004).

Cellulose acetate is produced in three main phases, including activation, acetylation, and hydrolysis. Currently, all industrial processes produce completely substituted cellulose tri-acetate with a substitution degree of 2.9 as the primary product (Baldino and Reverchon 2021). Then, cellulose tri-acetate is isolated and partially de-substituted to obtain secondary cellulose acetate with a substitution degree of 1.8 to 2.5 (Tsunashima and Hattori 2000).

Commercial processes for the production of cellulose acetate basically depend on the reaction of activated cellulose by acetic anhydride with use of a strong acid catalyst. The term “activated cellulose” is employed to describe any form of increased accessibility of cellulose through any pretreatments intended to make the cellulose more soluble in specific media or more reactive in chemical reactions (Heinze *et al.* 2018). The rate and yield of the acetylation reaction, *i.e.*, the adequate substitution of the acetyl functional group with hydroxyl groups located in the C-2, -3, and -6 positions in cellulose are strongly dependent on the availability or accessibility of these OH groups.

From a traditional chemical perspective, hydroxyl group esterification appears relatively straightforward; however, the unique morphology of the cellulose fiber presents challenges that require unique chemical processing techniques (Balser *et al.* 2004). Some effective structural parameters in the reactions of cellulose include the arrangement and configuration of pores and voids, the structure of the fibrils, the degree of crystallinity, and the extent of the different hydrogen bonds (Schleicher and Kunze 1988). It has been suggested that the total volume of micropores, pore size distribution, and internal surface area in swollen fibers correlates closely with acetylation reactivity (Nelson and Oliver 2007). Actually, cellulose structure can be considered a matrix channeled by a system of pores and voids that are at least partially interconnected, with a continuous distribution range of diameter down to atomic dimensions with the possibility of shifts in their size distribution by the swelling process itself (Philipp *et al.* 2007). During industrial processing, some formation of irreversible bonds between cellulose microfibrils interpreted microfibril aggregation has been reported (Pönni *et al.* 2013). Additionally, there are two secondary hydroxyl groups to each primary group per glucose anhydride unit, for which two-thirds of the total cellulose is expected to react by the slower process and one- third by the faster (Hiller 1953). In contrast, the noncrystalline and crystalline phases of cellulose behave differently in confronting chemical reagents that diffuses in the former while for the latter it requires to first react at the chain ends or on the surface of the crystallites resulting in the opening or unzipping of some of the hydrogen-bonded chains of cellulose, thus producing some amorphous cellulose. Therefore, the phenomenon is extremely complex, and the kinetics cannot be treated either as a simple chemical process or as a simple diffusion process. Both processes are concurrently occurring, and they are dependent on each other (Chatterjee and Conrad 1967). Finally, among the parameters related to the penetrating liquid, molar volume, acidity, and dipolarity/polarizability (Heinze *et al.* 2018), as well as the solubility parameter (Philipp *et al.* 2007).

Considering the quasi- or entirely macroheterogeneous nature of cellulose reactions (Chatterjee and Conrad 1966), the aforementioned review of literature aimed to emphasize the complexity of the process and thus the importance of assigning adequate scientific scrutiny for re-studying the mechanism of cellulose activation despite many classical experiments being published. Moreover, plant-based materials have re-gained comprehensive attention as integral parts in transitioning to a circular economy (Shogren *et al.* 2019). Additionally, the subject of reactivating and functionalizing cellulose for enhancement in its roles in the synthesis of novel multifunctional and bio-based materials has been categorized in recent studies (del Cerro *et al.* 2020; Ferreira *et al.* 2020; Wu *et al.* 2020)

Divergent approaches (Li *et al.* 2018) have been applied to increase the reactivity of dissolving pulp, including mechanical treatment (McKenzie and Higgins 1956; Alekseeva *et al.* 1997), enzymatic treatment (Wu *et al.* 2020), caustic extraction, ionic liquid extraction (Hanabusa *et al.* 2018), acid treatment, ozone treatment, thermal degradation, and some non-conventional methods and materials (Beaumont *et al.* 2020, 2021; Liu *et al.* 2019; Zhou *et al.* 2019). The targets of these methods incorporate surface area expansion through a) widening of pores, cavities, and inter-fibrillar interstices, b) disruption of fibrillar aggregation, and decreasing the sizes of the crystallites, and c) changing the crystalline structure by conversion of cellulose I to cellulose II, which affect both inter-crystalline and intra-crystalline swelling (Heinze *et al.* 2018).

The result of activation process performance is the enhanced availability of cellulose hydroxyl groups for acetylation. Swelling rate is a function of the swelling of cellulose fibers, cellulose orientation, temperature, and time. For example, if a small molecule is polarized, the movement would be easy, and it can also release pressure from the secondary capacity and finally create the highest swelling. Water is an ideal swelling agent (in terms of molecular size and polarity); however, water consumes acetic anhydride for acetylation, and for this reason it is not an ideal solvent for the activation of cellulose acetate. In most cases, acetic acid is used as an effective swelling agent similar to water, but with less propagation velocity. Today, only the “Acetic Acid Process” is of industrial importance and relevance (Hummel 2004), and therefore other activation process are not investigated in the current literature. Formic acid gives greater activity but introduces undesirable formyl groups that have to be replaced later. Thus, among the lower aliphatic acids, acetic acid is the best practical activating liquid (Malm *et al.* 1952). Among all existing methods for the activation of cellulose to produce cellulose acetate, using sulfuric acid as a catalyst with acetic acid in the swelling agent liquid is recommended. Sulfuric acid is probably used to rupture the hydrogen bonds and then to increase the swelling. Moreover, using sulfuric acid together with acetic acid reduces the time of swelling of cellulose fibers in the activation procedure (Malm *et al.* 1958; Cheng *et al.* 2010; Luo *et al.* 2013).

Considering the importance of the activation step to achieve effective and economic acetylation, this study focused on the factors influencing the activation phase (acetic acid concentration, time, and amount of catalyst). Based on the authors’ knowledge, no recent study has explored the activation phase extensively, and hence results of this research can represent novel data. Additionally, the measured activation parameters are well recommended for future studies on cellulose activation to evaluate the suitability of the product for new and novel derivatives.

EXPERIMENTAL

Materials

Raw material as bleached alpha cellulose pulp was supplied by Parchin Chemical Industries (Tehran, Iran). First, moisture content of the samples was determined according to TAPPI T412 om-11 (2011). Other properties of this pulp are shown in Table 1.

Table 1. Properties of Alpha Cellulose (Control Sample)

Moisture Content (%)	**Alpha Cellulose** (%)	**WRV** (g/g)	**Carboxyl Groups** (mmol/kg)	**Cupper Number** (0.1)	**Reactivity** (%)	**Viscosity** (mL/g)
4	98	0.52	44.6	0.1	0.51	926

WRV: Water retention value

The cellulose activation process to prepare samples for acetylation phase was conducted at 5% consistency at a temperature of 35 ± 2 °C and three reaction times (*T*) of 30, 60, and 90 min in a shaking incubator (JAL TEB, Tehran, Iran). Pure acetic acid (C) as the activation agent was used in three addition levels of 25, 35, and 45 units to 100 units of dry alpha cellulose. Additionally, sulfuric acid of 95% (H) as a catalyst was used in four addition levels of 0, 0.1, 0.5, and 1% proportional to the concentration of acetic acid. These values correspond to traditional literature (Malm *et al.* 1952), where the temperature ranges from 20 to 38 °C, activation time ranges from 10 to 360 minutes, and the sulfuric acid catalyst addition levels ranges from 0 to 0.067 moles per 100 grams of linter. Finally, the properties of activated cellulose were determined with four laboratory tests including: 1) Evaluation of water retention value (WRV) according to TAPPI UM 256 which include a representative specimen with 1400 g/m^2 on an oven-dry fiber basis, with a relative centrifugal force (RCF) of 900 G, and a centrifuge duration time of 30 min (2011); 2) Measurement of the reactivity of alpha cellulose by determination of alkali adsorption at fibers soaked in alkali solution like potassium hydroxide (KOH) due to uniform distribution of this alkali within fiber (Jaturapiree *et al.* 2008); 3) Determination of carboxyl groups with the absorption of methylene blue (Klemm *et al.* 1998); and 4) Determination of viscosity according to ASTM D871-96 (2010). The chemical structure and the crystallinity of a cellulosic fiber was studied by Fourier Transform Infrared (FTIR) spectroscopy FT/IR-4700, JASCO International Co., Ltd., Tokyo, Japan. For each treatment, three replicates were used and the results were subjected to analysis of variance followed by the Duncan test. Activated cellulose properties were compared statistically using a protected Duncan test ($p \leq 0.05$) followed by one-factor analysis of variance (ANOVA), using IBM SPSS (IBM Corp., v.17, Armonk, NY, USA) statistics 21 procedures.

RESULTS AND DISCUSSION

Analysis of Water Holding Capacity of Activated Pulp

Water retention value (WRV) has been traditionally utilized to determine the accessibility of alpha cellulose as a criterion to evaluate its potential for cellulose derivatives production (Pönni *et al.* 2013; Aïssa *et al.* 2019).

As shown in Fig. 1a, in a 25-unit consumption of acetic acid, increasing the pre-activation time with each consumption level of catalyst resulted in a significant increase of WRV. It has already been proposed (Chatterjee and Conrad 1967) that diffusion process rules the access of liquids both to amorphous and crystalline regions of cellulose by two independent rates of diffusion and of chemical reaction in which diffusion as the slower one becomes the rate-governing or pace-setting rate. Therefore, for the proper diffusion of chemical reagent into the crystalline region, the chain ends or the surface of the crystallites have to be reacted by the chemical regent that results in unzipping or the detachment of some of the hydrogen-bonded chains of cellulose, thus producing some more amorphous cellulose. The reagent then diffuses into this newly produced amorphous portion, reacting with the cellulose and simultaneously generating more amorphous cellulose. Both processes are concurrently occurring and they are dependent on each other. It was indicated that the rate of diffusion and the extent of swelling in cellulose are functions of the swelling agent, cellulose state, temperature, and time (Rosenthal 1967).

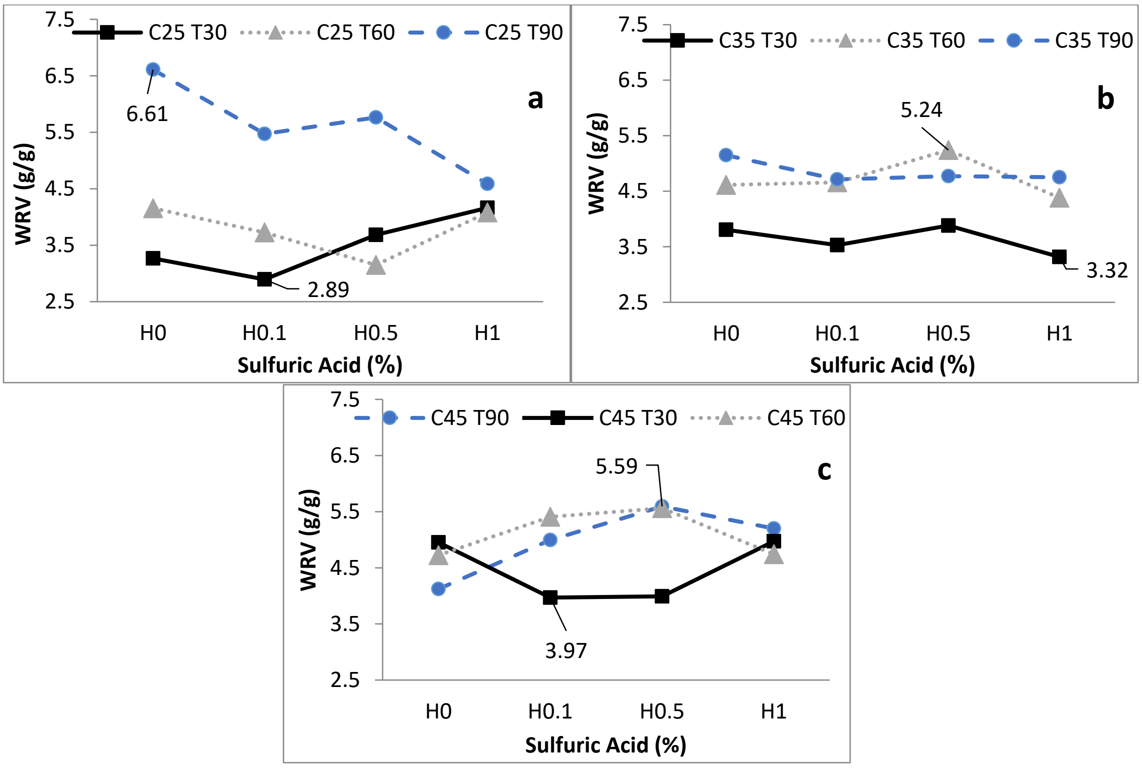

Fig. 1. WRV of activated cellulose pulp from cotton linter in three addition levels of acetic acid (1a. C25, 1b. C35, and 1c. C45) and four addition levels of sulfuric acid ranging 0, 0.1, 0.5 and 1% designated H0, H0.1, H0.5 and H1, respectively

At low addition levels of acetic acid (Fig. 1a), *i.e.*, 30 and 60 min, the sulfuric acid addition level was more pronounced in making more accessible sites in cellulose than with a longer time of 90 min. In addition, it is inferred from Fig. 1 that as a kinetic component, the effect of time as a variable is more perceptible in lower dosages of acetic acid. According to Fig. 1, the treatment of C25T90H0 (denoting a treatment with 25 units of acetic acid to 100 units of dry alpha cellulose, 90 °C of temperature and 0% addition level of sulfuric acid) had the highest WRV due to gradual activity of the acetic acid in cellulosic fiber swelling in the absence of sulfuric acid, which had likely the potency for the removal in the highly accessible and hygroscopic amorphous regions of cellulose (Malm *et al.* 1958) as illustrated in the declining trend in WRV especially in 90 min with the lowest value in the maximum 1% catalyst consumption. It should be noted, however, there was no significant difference between the highest measured WRV and the treatments of $C_{25}T_{90}H_{0.5}$, $C_{45}T_{90}$ $H_{0.5}$, and $C_{45}T_{60}H_{0.5}$.

As shown in Figs. 1b and 1c, with increasing acetic acid dosages (35 and 45 units) especially in the shorter time frames (30 and 60 min), compared to Fig. 1a, a higher WRV was achieved that was not plausible for 90 min. It is assumed that the proportion of acetic acid in the pre-activation process is more dominant than time as a variable because at a shorter time higher WRV was gained. It was observed that the system of reaction-diffusion in the presence of both organic and inorganic acids was inversely affected in both the low and high concentration of acetic acid. At the high dosages of acetic acid reaching to extreme swelling it was necessary to use higher addition levels of sulfuric acid (1%), while in the zero concentration of acetic acid (C25), the utmost WRV value was achieved. It has also already been found that the co-existence of acetic acid with sulfuric acid in the activation stage of cellulose prolongs the time required for complete swelling considerably. It was speculated that sorption of sulfuric acid on the outer surfaces of unswollen cellulose blocked the pore entrances into the cellulose structure either by actual physical blocking or by an electrical repulsion effect, thus reduced the cellulose swelling rate with a more pronounced effect at high dilutions of sulfuric acid in acetic acid due to selective sorption of sulfuric acid by the cellulose (Rosenthal 1967).

Conformed by Fig. 1, the inclusion of three variables of time and addition levels of acetic and sulfuric acids resulted in diverse values of WRV that can be justified considering the diffusion mechanism. It has been evidenced that the time dependence and final value of the swelling of cellulose in various liquids are determined by molar volume and the solubility parameter of liquid, both in the hydrogen bonding part and the polar part (Philipp *et al.* 2007) as well as in its basicity and dipolar character (El Seoud *et al.* 2008; Fidale *et al.* 2008).

Additionally, according to Fig. 1, despite being statistically significant, in most cases the differences were slight, necessitating exploitation of an alternative indicator to WRV for studying cellulose modifications and for a sound judgment to qualify the pulp for later processing to the final cellulose acetate.

Carboxyl Groups

Carboxyl groups are functional groups in cellulose fibers that have ionization ability and are important due to their chemical impacts on the fiber surface charge (Sjöström 1989; Zemljič *et al.* 2002). The carboxyl content of the fibers provides a relative indication of the swelling capability of the pulp. It is commonly conceded that enhanced fiber swelling relates to increased concentration of acid groups in the pulp and also there is a linear positive relationship with pulp WRV (Chen *et al.* 2013).

As Fig. 2 represents, the maximum amount of carboxyl groups was determined for the C25T90H0.5 treatment and the least amount was observed for the C25T60H0 treatment. According to the statistical results, no significant difference was revealed between the maximum value and the C45T90H0.5 and C25T90H0 treatments. Comparing WRV and the carboxyl groups graphs (Figs. 1 and 2) in activated alpha cellulose pulp indicated that almost anywhere that carboxyl groups were high, WRV increased. This was probably due to more incorporation of carboxyl groups in activation reactions with acetic acid. Considering Table 1, the control sample of alpha cellulose contained 44.6 mmol/kg of carboxyl groups probably originating from pulping and bleaching operations (Sjöström

1989), which at least increased 4% compared to the minimum value calculated the carboxyl groups of the C25T60H0 treatment. An aqueous mixture of acetic acid and sulfuric acid has already been reported to have partially esterified cellulose followed by the penetration of hydronium ions in the amorphous domains of cellulose chains promoting the hydrolytic cleavage of the glycosidic bonds and releasing individual crystallites (Tang *et al.* 2013). Additionally, the created carboxyl groups on the cellulose chains then possess activation and inductive effects on the cleavage of the 1,4-glycosidic bonds inside the cellulose chains (Zhou *et al.* 2015).

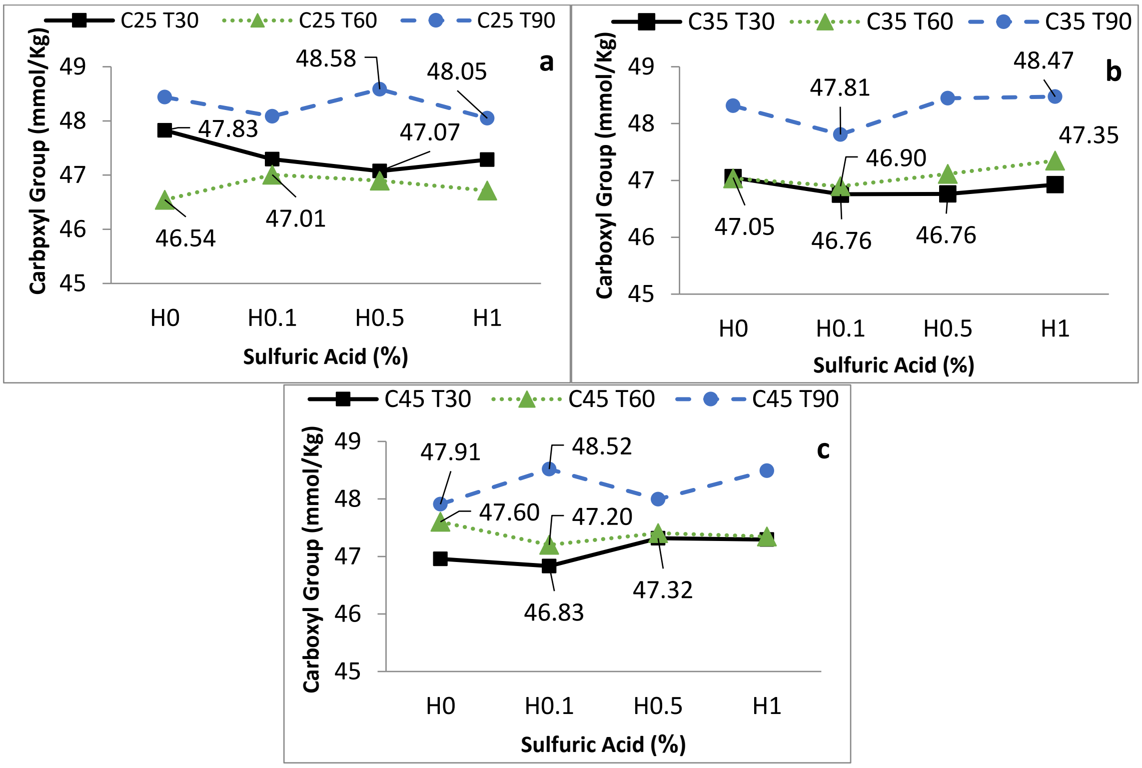

Fig. 2. Carboxyl groups content in activated alpha cellulose from cotton linter in three addition levels of acetic acid (1a. C25, 1b. C35, and 1c. C45)

Pre-activation by acetic acid has led to the internal swelling of cellulose (Rosenthal 1967). Because acetic acid possesses a carboxyl group in its chemical structure, it is assumed that in the pre-activation process, this group is replaced with hydroxyl groups on C2, C3, and C6 of the cellulose chain and proportional to the numbers of the replacements, higher numbers of carboxyl groups are added on the cellulose chain. In the meantime, increasing the pre-activation time especially in higher addition levels of acetic acid (Figs. 2a and 2b) as well as adding the catalyst consumption dosage caused the improvement of carboxyl groups in a logical trend. It is assumed that due to the degradation of the cellulose chain structure assisted by the presence of the sulfuric acid catalyst, the dominant replacement took place on C2 and C3 (Zemljič *et al.* 2002). This is not conclusive, but in many cases the viscosity has been reduced proportional to the increase of carboxyl groups (Fig. 3b and 3c), which accords with this finding.

Viscosity

In cellulose acetate production, the cellulose chain length should be considerably shorter than the original cellulose chain to be soluble in organic solvents in the subsequent processing steps to be able to create the solution with optimal viscosity appropriate to its commercial applications (Malm *et al.* 1952).

A requisite consequence of diverse cellulose activating processes is the cleaving of hydrogen bonds among the fibrils in a more or less large extent. Through this cleaving, the reagent transport is improved for the subsequent reactions, the reaction proceeds presumably faster and/or more uniformly, and additionally energy for the breakage of the bonds between the fibrils is needed in a lesser extent. The alternations of the bonds between the fibrils are characterized by the decrease of the level-off degree of polymerization (DP) of the cellulose. Through the various pulping processes and activating treatments, the cellulose structure is changed in a different way (Schleicher and Kunze 1988). The degree of polymerization and viscosity values are interrelated and are calculated accordingly (Sihtola 1963). Changes in the viscosity of activated alpha cellulose from the cotton linter in three addition levels of acetic acid are illustrated in Fig. 3.

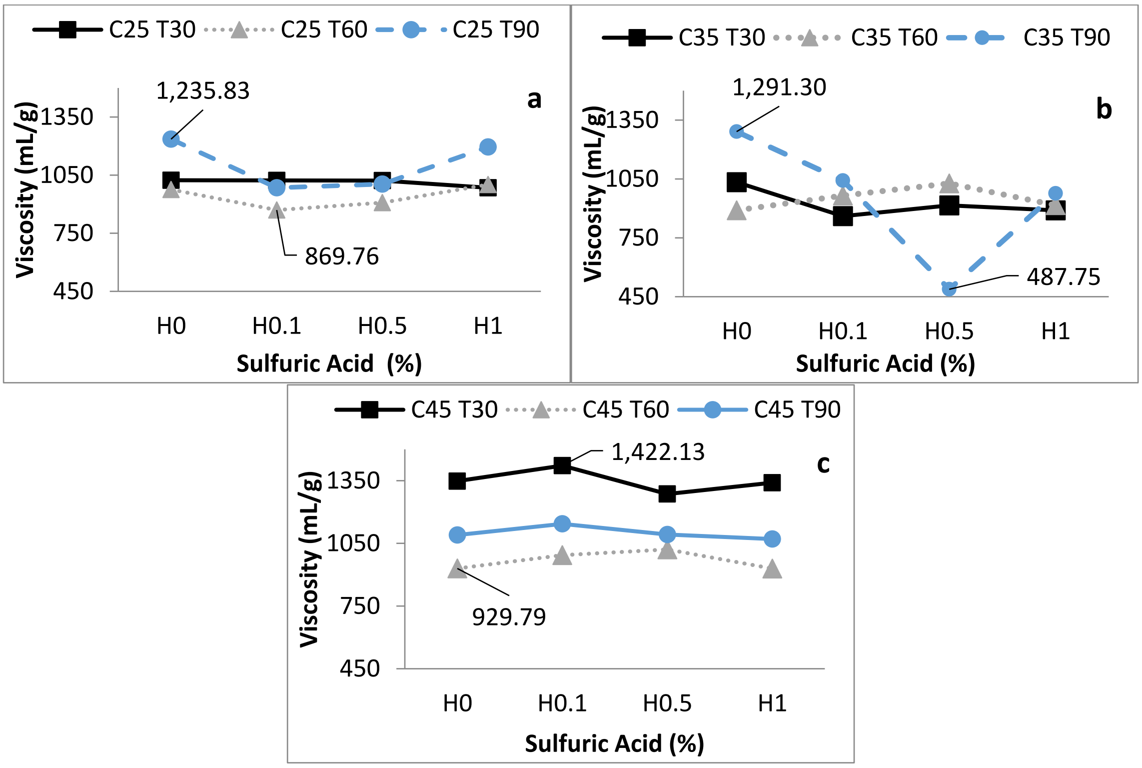

Fig. 3. Viscosity of activated alpha cellulose from cotton linter in three addition levels of acetic acid (1a. C25, 1b. C35, and 1c. C45)

As shown in Fig. 3(c), the maximum value of the viscosity was achieved by the C45T30H0.1 treatment, and the least amount of this value was related to the C35T90H0.5 treatment. As implied by this result, increasing the pre-treatment time caused the reduction in viscosity. It should be noted that the other treatments of C45T90H0.5, C45T60H0.5, and C25T90H0 had no significant difference with C45T30H0.1.

The results implied by the Fig. 3 reveal that addition levels of both regents, especially acetic acid, do not necessarily reduce the viscosity. It is necessary to mention that acetic acid activation energy does not break down the cellulose chains and presumably, the catalyst promotes the cleavage of hydrogen bonds and, thus, both act as swelling agents and cause the increase in the accessibility of cellulose. It has already been reported that a small amount of catalyst reduces the chain length; however, the amount of catalyst is not as important as uniform distribution on the molecular weight of cellulose (Rosenthal 1967).

In addition, as disclosed by Fig. 3, in some cases viscosity was increased by increasing the pre-activation time together with the acid catalyst; *i.e.*, in acetic acid containing sulfuric acid the time required for complete swelling was prolonged. The explanation of this occurrence has been speculated to be due to the sorption of sulfuric acid on the outer surfaces of unswollen cellulose and the blockage of the pore entrances into the cellulose structure either by actual physical blocking or by an electrical repulsion effect, thus reducing the cellulose swelling rate particularly at high dilutions of sulfuric acid in acetic acid because of the selective sorption of sulfuric acid by the cellulose (Rosenthal 1967).

Based on a comparison of Fig. 1c and Fig. 3c, the conditions of 60 min (T60) with the maximum dosage of acetic acid (C45) could be selected as the optimal treatment for the acetylation phase because if minimum activation time is satisfied, the cuprammonium viscosity values are lower and measure the cellulose breakdown. If not, higher values are obtained, which indicate nonuniform activation (Malm *et al.* 1952).

Reactivity

Accessibility and reactivity of cellulose fibers are notable features of cellulose fibers that represent the activity of fibers in chemical reactions. Among the different alkali types, KOH solutions appear to have a more uniform distribution within fibers (Jaturapiree *et al.* 2008). Additionally, the measurement of this alkali retention value is expected to give different results compared to WRV, as observed in comparison of Figs. 1 and 3, and it, therefore, offers more indicative results for better judgment about the accessibility and hence reactivity.

To discriminate the accessibility and reactivity, it should be noted that the reactivity of cellulose treated with swelling agents is dependent on the type of swelling achieved with respect to inter- and intra-fibrillar swelling during the process and not only on the degree of swelling (Warwicker and Clayton 1969). It has been reported that the swelling of cellulose by alkaline solutions is correlated with base concentration, the hydrated radii of the alkali metal ions, and the temperature (Fidale *et al.* 2008).

As shown in Fig. 4a, in the low addition level of acetic acid (25 units), the highest activity was reached in a short time frame (30 min) and by increasing the pre-activation time, the reactivity was diminished. In this case, the highest reactivity was obtained with 0.5% catalyst (C25T30H0.5). However, statistical analysis revealed no significant difference between C25T30H0.5 and the other treatments of C45T90H0.5, C35T30H1, and C25T30H0.

In 35 units of acetic acid consumption, no certain trend for reactivity was observed, but the maximum value was reached in C35T30H1. However, the best trend of reactivity was recognized in the 45 unit of acetic acid consumption, displaying the increase in reactivity due to the increase of pre-activation time, of which the highest value was observed in C45T90H0.5. Therefore, it is implied that the concentration of acetic acid as well as the concentration of the acid catalyst have both the influence to change the reactivity as by increasing their concentration and the destruction of the amorphous part of cellulose; the reaction time decreases so that the maximum value of reactivity is reached in C45T90H0.5.

Eventually, similar to WRV, the results of KOH sorption did not replicate the trends in carboxyl content and viscosity. It was already elucidated that differences in the molecular structure, including the degree of polymerization or the carboxyl content, had no or only a minimal effect on the reactivity of cellulose that was mainly influenced by the structure of the pores and fibrils as well as by the system of the hydrogen bonds but in a different way for the different reactions (Schleicher and Kunze 1988).

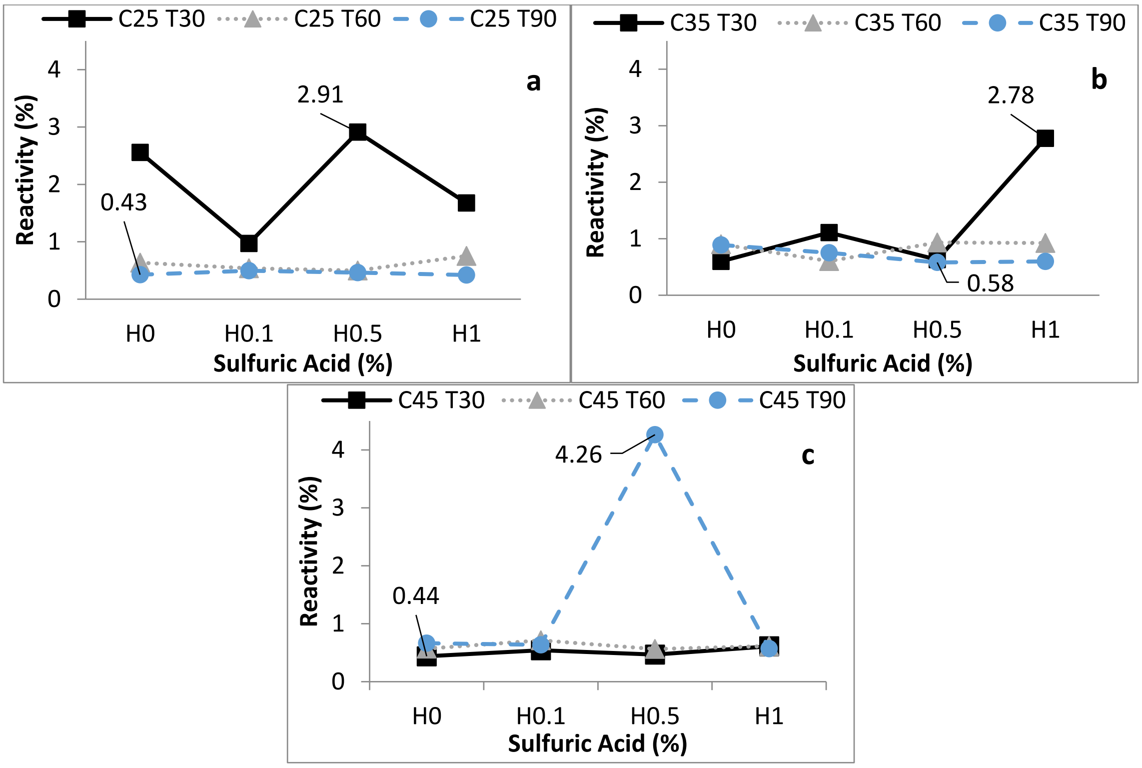

Fig. 4. Reactivity of activated alpha cellulose pulp from cotton linter in three addition levels of acetic acid (1a. C25, 1b. C35, and 1c. C45)

FTIR Spectroscopic Analysis

Fourier transform infrared spectra of control alpha cellulose pulp and the selected samples of higher reactivity and swelling are presented in Figs. 5 and 6, respectively.

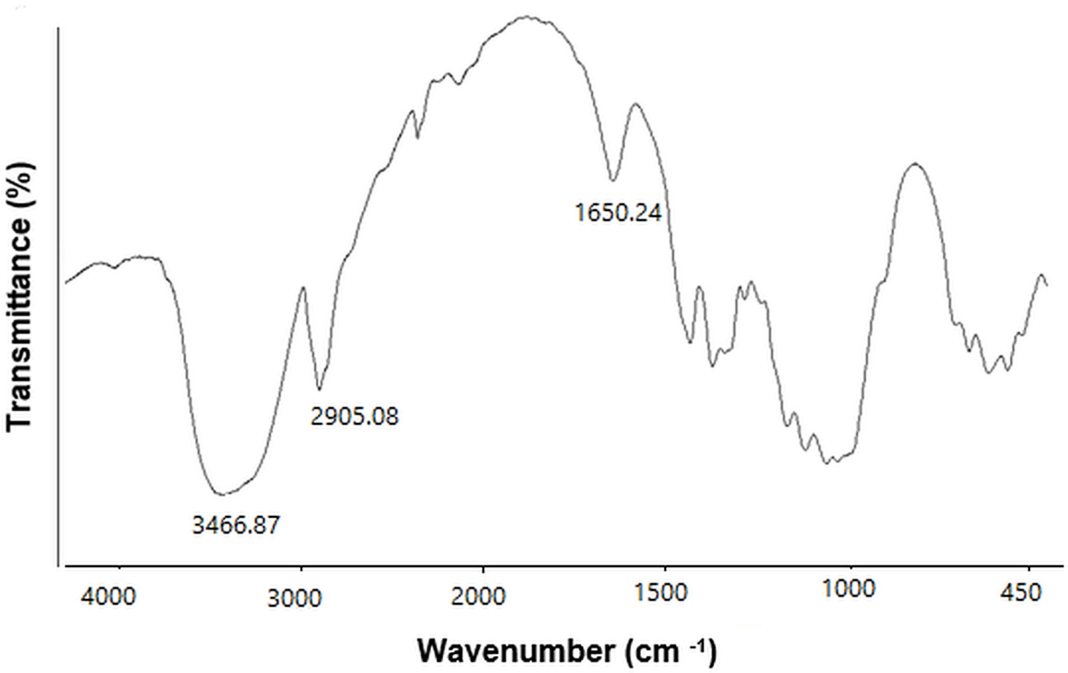

Fig. 5. FTIR spectrum of control alpha cellulose pulp

The observed peaks in the wavenumber range of 3660 to 2900 cm^{-1} is characteristic for the stretching vibration of O-H and C-H bonds in polysaccharides. These peaks include inter- and intra-molecular hydrogen bond vibrations in cellulose (Hospodarova *et al.* 2018). The alpha-cellulose spectrum in Fig. 5 shows peaks at 3466.87 cm^{-1} (O-H stretch) and 2905.08 cm^{-1} (C-H sp3 stretch). The band at 2905 cm^{-1} is attributed to CH stretching vibration of all hydrocarbon constituents in polysaccharides. The peaks at 1633 cm^{-1} correspond to the vibration of water molecules absorbed in cellulose (Hivechi *et al.* 2015). The corresponding peak in the current control sample was determined as 1650.24 cm^{-1}. Typical bands assigned to cellulose were observed in the region of 1630 to 900 cm^{-1}, the so-called fingerprint region (Phinichka and Kaenthong 2018). The absorbance bands appearing between 1500 and 890 cm^{-1} can be assigned to stretching and bending vibrations of the $-CH_2$ and -CH, -OH, and C-O bonds in cellulose. The presence of lignin was characterized by adsorbed peaks at 1500 to 1600 cm^{-1} and 1220 cm^{-1} due to aromatic C=C and C-O phenolic bonds (Hivechi *et al.* 2015).

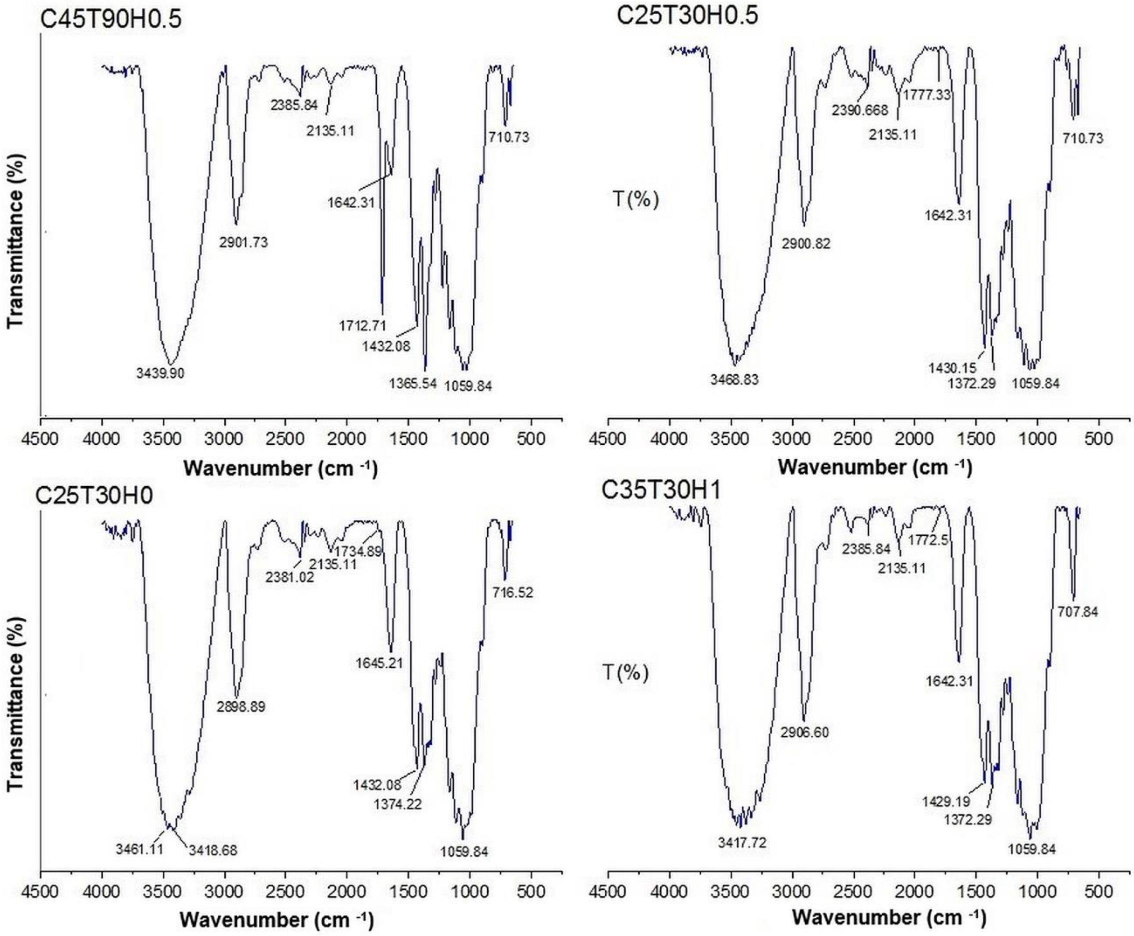

Fig. 6. FTIR spectra of some treated alpha cellulose fibers selected based on WRV and reactivity

Figure 6 compares the changes in the bands of the selected treatments based on the higher values determined for WRV and reactivity. Practically the same absorbance peaks shown in the cellulose fibers were also observed in the spectrum of different treated fibers. These absorbances were almost consistent with those of the alpha cellulose pulp backbone with some slight differences, emphasizing that the structure of cellulose had not been damaged after the treatments. Activated alpha cellulose pulps showed peaks of 1777.33, 1734.89, 1772.5, and 1713.06, which are attributed to carboxyl functional groups indicating the successful effect of the pre-activation treatment together with an increase in the intensity of the C–H band in the range 3000 to 2800 cm^{-1} (Tang *et al.* 2013). As noticed, the treatment of C45T90H0.5 denotes the adjoining of the highest carboxyl groups that corresponds with the results of Fig. 2. As previously mentioned, the band of 3466 cm^{-1} was indicative for hydroxyl groups that reached to 3417 and 3435 cm^{-1} after pre-activation. This change in the intensity of OH peaks may be due to the liberation of OH groups from the interaction (*e.g.*, hydrogen bonding) with the impurities, such as lignin (Shaheen and Emam 2018) or the shifts in hydroxyl groups towards carboxyl groups, which encourage the enhancement of alpha cellulose pulp reactivity in the subsequent processes confirmed by the results of Fig. 4.

It has already been reported that peaks between 750 and 1000 cm^{-1} and also other peaks around 1350 and 1175 cm^{-1} indicate the presence of sulfonates (Morais *et al.* 2013).

The bands close to these numbers were recorded in the FTIR spectrum of the treated samples. The peak at 1059.84 cm^{-1} was attributed to C-C stretching (Wang *et al.* 2020).

The diffusion of reagents and the consequent swelling of cellulose fibers is controlled by the relative amount of crystalline material in cellulose, which is termed as the crystallinity index (CI). Fourier transform infrared spectroscopy determines CI by measuring relative peak heights or areas (Park *et al.* 2010). The change of a cellulose crystal structure leads to a simplification of the spectral contour through a reduction in intensity or even the disappearance of the bands characteristic of the crystalline domains. Comparing the spectrum of control alpha cellulose pulp with the spectra of the treated fibers, it is evident that less energy absorbed due to the CH_2 bending at the bands at around 1420 to 1430 cm^{-1} of the treated samples spectrum known as the “crystallinity band” (Matheus *et al.* 2014). Therefore, a decrease in its intensity will reflect the reduction in the degree of crystallinity of the treated samples. In contrast, it has already been outlined that the absorbance band at around 894 to 898 cm^{-1} is assigned to C-O-C bridge stretching, which is designated as the “amorphous” absorbance band (Åkerholm *et al.* 2004; Boukir *et al.* 2019). The treated samples (Fig. 6) showed no record of this band highlighting the possibility of substantial removal of the non-crystalline region in the presence of both organic and inorganic acids.

The absorbance peak at around 1700 cm^{-1} was associated with carboxylic groups in acetic acid byproduct (Tang *et al.* 2013; Araújo *et al.* 2020). Moreover, when the hydroxyl group of cellulose is oxidized to aldehyde (-CHO) or carboxylic acid (-COOH) group, an identical peak at 1760 cm^{-1} appears (Rahman *et al.* 2016). These absorbance bands are well matched with the results presented in Fig. 6.

CONCLUSIONS

This research studied the activation of functional groups in the cellulose chain using acetic acid in the presence or absence of sulfuric acid catalyst for the preparation of activated alpha cellulose pulp, which is subsequently used in the acetylation phase of cellulose acetate production. According to the results, the following conclusions were obtained:

1. The activation of cellulose using only acetic acid with varying concentrations caused the improvement of the properties of cellulose for the acetylation phase.
2. The addition of sulfuric acid catalyst to acetic acid led to a loss in viscosity of the cellulose chain but considering the improvement of other cellulose properties with acceptable loss of viscosity, the suitable amount of catalyst consumption was determined to be 0.5% in this phase.
3. It was implied that in some cases the use of acid catalyst resulted in cellulose oxidation and the replacement of carboxyl groups of acetic acid on C6 of the cellulose chain. This caused the subsequent enlargement in molecular weight that was revealed as the prolongation of time required for complete swelling due to the catalyst effect.
4. The results indicated simultaneous/interaction effects of independent variables including pretreatment time, acetic acid, and catalyst consumption levels on the responses of WRV, carboxyl groups content, viscosity, and reactivity in activated alpha cellulose. Concurrent increase of catalyst addition level in high temperature (T90),

displayed a descending trend in WRV in low acetic acid (C25) and ascending trend in WRV in high acetic acid (C45). Carboxyl group's content in activated alpha cellulose was most affected by temperature and less affected by other variables and finally in high levels of acetic acid (C45), temperature substantially affected the viscosity with more pronounced influence than the catalyst addition levels.

5. In the pre-activation process, acetic acid and catalyst consumption levels are more influential than the treatment time. Therefore, by controlling them, the raw pulp is more appropriately prepared for the next acetylation process.
6. The system of reaction-diffusion in the presence of both organic and inorganic acids is inversely affected in both the low and high concentration of acetic acid in the manner that in the high dosages of acetic acid reaching to extreme swelling required higher addition levels of sulfuric acid (1%), while in the zero concentration of acetic acid (C25), the utmost WRV value was achieved.
7. Based on the results, especially reactivity, C45T90H0.5, C25T30H0.5, C25T30H0, and C35T30H1 treatments are suggested for acetylation phase in the cellulose acetate production, in the order of priority.

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