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Physicochemical properties of delignified hemp fiber cellulose acetate (HFCA)

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Abstract

Cellulose acetate (CA) is an important material with commercial and industrial applications, such as coatings, films, and membranes. The reaction of cellulosic hydroxyl groups (-OH) in delignified hemp fiber with acetic anhydride and glacial acetic acid afforded hemp fiber cellulose acetate (HFCA). The HFCA yield was determined to be 128.1%, where an increase in yield and gain in sample mass corresponds to the transformation of the hydroxyl group to a heavier acetyl group during the esterification process. Acid-base titration was conducted to measure the relative amount of acetyl groups (% acetyl) introduced in the delignified hemp fiber cellulose chain and the degree of acetate substitution (DS). FTIR was used to verify the delignification and esterification processes, through the appearance and disappearance of signature peaks. DSC was used to determine the change in the rigidity of HFCA by observing the decrease in crystallinity and increase in amorphous character (T_g) at 134.3 °C. Meanwhile, TMA was employed to determine changes in dimensional stability by observing the softening temperature (T_s) at 131.8 °C. TMA and DSC were used to determine the melting temperatures (T_m) of HFCA at 220.9 °C and 206.7 °C, respectively.

Keywords: *Delignification, Esterification, Hemp fiber, Cellulose acetate, Thermomechanical analysis.*

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1. Introduction

Hemp is a natural fiber from plant stems (*Cannabis sativa* L.) likened to linen, ramie, flax, and bamboo which has numerous uses and applications in textiles, films, and plastics industries. Hemp fiber is structurally composed of cellulose, hemicellulose, and lignin. Cellulose is the major component of plant fibers and is considered to be the most abundant organic polymer in nature. It is a polysaccharide composed of repeating units of glucose monomers assembled in crystalline and amorphous regions (Poletto et al., 2014). Cellulose is one of the most important organic polymers worldwide due to its availability and biodegradability. Hemp fibers are known for their property to impart strength and reliable adhesion between the matrix and cellulose fiber enhancing the features desirable for commercial and industrial uses (Ouajai & Shanks, 2005). Cellulose is also desirable due to its reactivity and ease of modification. The availability of three hydroxyl (-OH) groups in each glucose molecule make it reactive to chemical treatment designed to modify its natural properties or apply specific functionalities to the cellulosic fibers (Roy et al., 2009).

Cellulose is predominantly hydrophilic due to the presence of hydroxyl groups, especially in the amorphous regions where water molecules can easily access it. Several researchers developed ways to improve the hydrophobicity of cellulose by reacting and replacing the hydroxyl groups with chemical modifications such as cellulose esterification (He et al., 2014; Hamed et al., 2021; Tabaght et al., 2023; Sharma et al., 2024)). Esterification of cellulose involves the reaction of hydroxyl groups in glucose monomers with acetic anhydride and acetic acid to form a cellulosic ester (cellulose acetate, CA). The produced CA can be used in a variety of applications where water is avoided, such as food packaging, biomedical uses, filtration membranes, and waterproof paints and textiles, since it is more hydrophobic compared to the original cellulosic biomass (Das et al., 2014; Akartasse et al., 2022; Benahmed et al., 2022).

In this study, lignin was removed from the hemp fibers (delignification) followed by esterification of the resulting hemp cellulosic fibers to produce hemp fiber cellulose acetate (HFCA). The acetyl content and degree of acetate substitution of HFCA were determined through titration, the starting biomass and products were characterized through FTIR, and the mechanical properties and dimensional stability were quantified using Thermomechanical analysis (TMA) and Differential Scanning Calorimetry (DSC).

2. Materials and methods

2.1. Moisture content

The moisture content of ground hemp fibers was analyzed by placing (~3 g) samples on the weighing platform of the HB43-S Halogen Moisture Analyzer (Mettler Toledo, Columbus, OH, USA).

The moisture content was used to calculate the cellulose acetate yield on an oven-dry (OD) basis.

2.2. Delignification

The hemp fiber sample (15.0 g) was weighed into a 500 mL conical flask. Commercial bleach (7% NaOCl) was diluted to 1% and added (400 mL) to the conical flask containing the sample. The flask was then simmered on a hot plate for 2 hours and let cool slowly to room temperature for a week. After cooling, the delignified hemp fiber sample was washed with deionized water several times and left to stand for several minutes between washes, until the smell of chlorine dissipated. The washed sample was vacuum filtered after the final washing to recover the delignified fibers and then placed in an oven (105 °C) overnight.

2.3. Esterification

The moisture content of the delignified hemp fiber sample was determined using the method stated in section 2.1. The sample was then weighed (4.0 g) into a 250 mL conical flask and kept in an ice bath. Acetylating compounds (16.4 mL acetic anhydride, 16. 48 mL glacial acetic acid, and finally 0.34 mL concentrated sulfuric acid) were added slowly and dropwise via Pasteur pipette to the sample in the flask with occasional swirling. The opaque pasty product obtained after considerable swirling of the flask was kept for 72 hours.

The product was poured into a 500 mL beaker containing ice water to cool it down then decanting the supernatant liquor. The precipitated product was washed with deionized water 5 more times. The precipitated hemp fiber cellulose acetate (HFCA) was collected and vacuum-dried in an oven for 3 days.

2.4. Fourier-transform infrared spectroscopy (FTIR) analysis

The FTIR was calibrated first by running a background spectrum before running the samples (to compensate for the effects of air on the IR readings). A small amount of the samples (original hemp fiber, delignified hemp fiber, and hemp fiber cellulose acetate) were placed on the ATR crystal (ZnSe) on the Nicolet iS5 FTIR spectrometer (ThermoFisher Scientific, Madison, WI, USA), and a spectrum was collected.

2.5. Thermomechanical analysis (TMA)

The TMA analysis of the commercial CA and HFCA samples was performed using a PerkinElmer TMA 7 Thermomechanical Analyzer (PerkinElmer, Waltham, MA, USA) and initiated by forming a molded disc specimen. This was attained by weighing approximately 2.0 g of sample and transferring it into the compression molding matched barrel and plunger using a 30-ton hydraulic hot press (PHI). The sample was pressed at 180 – 200 °C and 1 – 2 tons into a disc measuring approximately

25 mm in diameter and 0.2 mm thick. A small portion of the disc (3 – 5 mm^2) was obtained, thickness measured by a caliper, and placed in the sample holder for the determination of T_s and T_m. The program temperature was set at 30 – 280 °C with a heating rate of 5 °C/min. The TMA data obtained was processed using Pyris v13.3 software.

2.6. Differential Scanning Calorimetry (DSC)

The DSC analysis was performed using a PerkinElmer DSC 7 Differential Scanning Calorimeter (PerkinElmer, Waltham, MA, USA). The commercial CA and HFCA samples (8 – 10 mg) were placed in the DSC sample pan for the determination of T_g and T_m. The program temperature was set at 30 – 280 °C with a heating rate of 10 °C/min. The DSC data obtained was processed using Pyris v13.3 software.

2.7. Acetyl content analysis

The degree of acetate substitution was determined by acid-base titration. A properly dried and ground HFCA (1.0 g) sample was placed in a 250 mL Erlenmeyer flask and 40 mL of 75% ethanol was added. The flask containing the sample was heated at 50 – 60 °C for 30 min. Afterward, 40 mL of 0.5 M NaOH solution was added by pipette and continued heating at 50 – 60 °C for an additional 15 min and then cooled down to room temperature and let stand for 3 d. The excess alkali was titrated against 0.5 M HCl using phenolphthalein as an indicator for both the sample and blank (ethanol solution). Commercial cellulose acetate was also analyzed for comparison. The % acetyl and the degree of acetate substitution (DS) were calculated according to the Standard Test Methods for Cellulose Acetate ASTM D 871-96 (American Society for Testing and Materials, 2004) using equations (1) and (2), respectively.

$$\%\,Acetyl = \left[\left(V_{NaOH,sample} - V_{NaOH,blank}\right)M_{NaOH} - \left(V_{HCl,sample} - V_{HCl,blank}\right)M_{HCl}\right] \times \frac{4.3}{w} \quad (1)$$

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

Where V = Volume (mL)
M = Concentration (M)
w = Sample (HFCA) weight (g)
DS = Degree of substitution

3. Results and discussion

The moisture contents of the original hemp fiber and the delignified hemp fiber were obtained using a moisture analyzer with a value of 4.5 ± 0.2 and 0.47 ± 0.06, respectively %. The first moisture content value was used to calculate the yield of delignified hemp fiber on an oven-dry basis. The second moisture content value (delignified hemp fiber) was necessary to calculate the yield of hemp fiber

cellulose acetate (HFCA) on an oven-dry basis. The moisture content of any wood or biomass (hemp fiber) sample can be calculated using equation (3).

$$mc = \frac{(W_g - W_o)}{W_o} \times 100\% \quad (3)$$

Where mc = Moisture content (%)
W_g = Green hemp fiber weight (g)
W_o = Oven dry hemp fiber weight (g)

Rearranging the variables in the equation, the W_o used for hemp fiber delignification and hemp fiber esterification were calculated and found to be 14.4 ± 0.1 and 4.0 ± 0.1 g, respectively. The delignification of hemp fiber was done by using commercial bleach (sodium hypochlorite). Sodium hypochlorite (NaClO) initiates oxidative bleaching on lignin, solubilizing the chromophoric polymer to low molecular weight monolignol fragments in the solution. This produces a colored supernatant and a semi-white residue (holocellulose moiety). The dissolved lignin was discarded and the resulting holocellulosic residue was washed several times until the dissipation of chlorine odors. The residue was then vacuum filtered to remove excess solution and water and dried in an oven overnight. The residual mass obtained after filtration and drying was 8.8 ± 0.1 g with an oven-dried yield of 58.9% (delignified hemp fiber). Table 1 summarizes the cellulosic contents (%) obtained from this study and comparisons with literature values. Other methods are available in the literature with regards to delignification, such as the more efficient but energy-intensive sodium chlorite – acetic acid method (70 °C for 6 h) and peracetic acid method which can be done at a relatively lower temperature at 25 °C for 48 h (Kumar et al., 2013).

Table 1. Cellulosic content of various feedstocks originating from hemp.

Sample	Cellulosic content (%)	Reference(s)
Hemp fiber (Delignified)	59	This study
Hemp stalk	70	Thomsen et al., 2005
Hemp core	34 – 44	Thomsen et al., 2005
Hemp bast	55 – 72	Thomsen et al., 2005

Cellulose acetate in general is an insoluble derivative of cellulose which is non-toxic and biodegradable. It is partially acetylated with degrees of acetylation occurring in random (29 – 45% acetyl content range) throughout the cellulose chain, forming cellulose mono-, di-, and triacetate (Kaur et al., 2018). Cellulose acetate is one of the most important cellulose esters alongside cellulose butyrate (CABs) and cellulose propionate (CAPs) due to its ease of synthesis, overall stability, and wide range applications such as films and coatings. The delignified hemp fiber was reacted with acetic anhydride

and glacial acetic acid with sulfuric acid as a catalyst to form hemp fiber cellulose acetate (HFCA). The calculated yield for HFCA after esterification was 128.1% (oven-dry basis). The observed increase in yield and sample mass (1.11 g) was due to the addition of acetyl groups on the cellulose chain, which were heavier in terms of molar mass compared to hydroxyl groups.

Cellulose esterification initially forms cellulose triacetate, wherein a subsequent step, water was added to halt the reaction and leads to partial hydrolysis of the triacetate. Cellulose acetate is a clear, tough, and flexible plastic. It is naturally resistant to weak organic and inorganic acids, non-polar oils, and solvents. Plasticizers can be used as additives to adjust and improve the flexible and rigid character of cellulose acetate. It can also be mixed with other types of cellulose esters, like CABs and CAPs, to enhance its moisture resistance (hydrophobicity) and overall toughness and flexibility. Figure 1 shows the reaction scheme forming cellulose acetate from cellulose (delignified fiber) as the starting material.

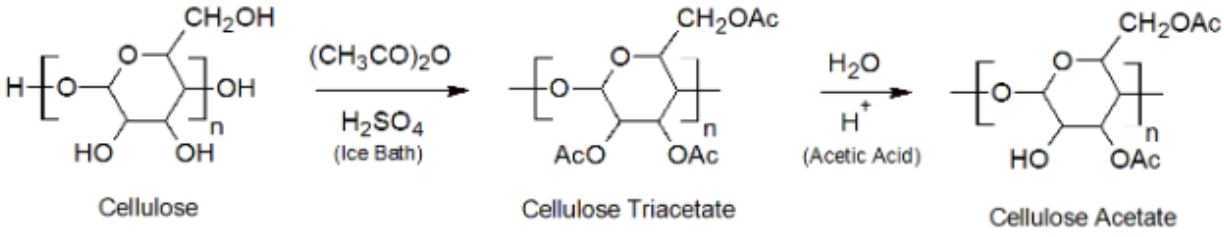

Figure 1. Formation of cellulose triacetate and subsequent hydrolysis to form cellulose acetate with cellulose as starting material reacted with acetic anhydride (Polymer Database, 2022).

The FTIR spectra of the original hemp fiber, delignified hemp fiber, and HFCA were obtained to verify the effectiveness of delignification by sodium hypochlorite and the degree of acetylation of cellulose present in the delignified hemp fiber. After delignification, there was an observed disappearance of peak at around 1500 (C=C str.) and 1050 cm^{-1} (C-C str.) due to the removal of phenolic monolignols and some of their branches and bonds (Gan et al., 2017). Meanwhile, after esterification of the delignified sample, a peak at 1750 cm^{-1} appeared corresponding to carbonyl stretching vibrations (C=O vib.). This confirms the formation of ester bonds after the reaction of cellulose with acetic anhydride. Esterification also led to the formation of a peak at around 1240- 1250 cm^{-1}, corresponding to the C-O stretching vibrations of the acetyl functional groups. Another prominent peak appeared at 1380 cm^{-1} attributed to the C-H bending vibrations of the methyl groups introduced (Özmen, 2012). The disappearance of the broad peak band at 3200 – 3500 cm^{-1} is mainly due to the removal of hydroxyl groups (-OH) and subsequent transformation to acetyl groups in the cellulose chain. Figure 2 shows the FTIR spectra showing the appearance of peaks validating the introduction of the peaks corresponding to cellulose acetate formation.

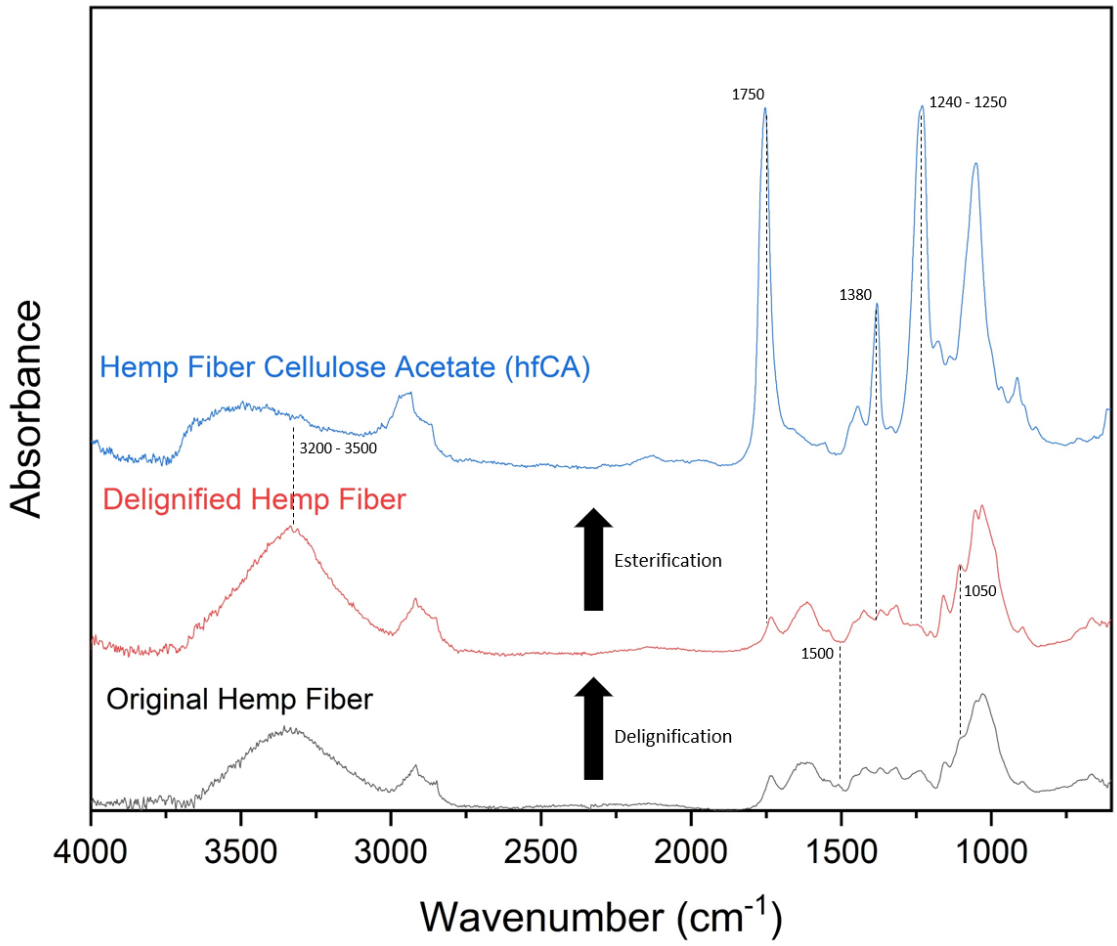

Figure 2. FTIR spectra of the original hemp fiber, delignified hemp fiber, and hemp fiber cellulose acetate (HFCA).

Thermomechanical analysis (TMA) was employed to determine the degree of deformation of the commercial CA and HFCA under the input of non-oscillating stress as a function of time or temperature. The change in thickness (expressed as % height) of the polymer disc prepared during TMA analysis was plotted as a function of temperature to determine softening temperature (T_s), at which a material exhibits considerable softening and abrupt changes in dimensions (Saba & Jawaid, 2018). Figure 3 shows the TMA thermogram of commercial CA and HFCA. The T_s values obtained for the commercial CA and HFCA were 135.39 °C and 131.8 °C, respectively. The softening of materials is an intermediate state wherein they transition from a rigid solid to being more pliable but still lack the ability to flow as a liquid. The TMA thermogram illustrates valuable information and insights on the dimensional changes, such as expansion and contraction of commercial CA and HFCA, as the material transitions from a rigid to a softened state under controlled heating and load.

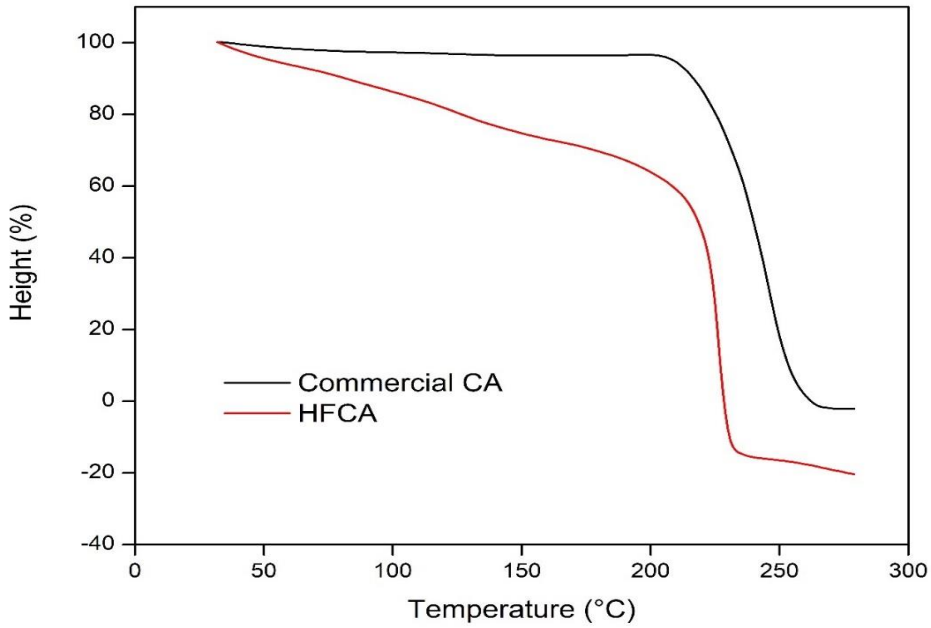

Figure 3. Thermomechanical Analysis (TMA) thermogram of commercial CA and HFCA.

The data obtained from FTIR and TMA analysis suggests the addition of acetyl functionality on the cellulose chain. DSC is another technique to demonstrate the chemical alteration of cellulosic fibers. Figure 4 shows the DSC thermogram of the commercial CA and HFCA. For HFCA, the residual hemicellulose after delignification of the fiber showed a broad endothermic peak from 50 – 200 °C, with a sharp peak at around 170 °C, followed by a broad exothermic peak from 170 – 200 °C. The exothermic peak was due to the decomposition of the amorphous regions of hemicellulose with subsequent formation of char (Kabir et al., 2013, 2021). The appearance of broad peaks signifies that hemicellulose, which contains amorphous -OH groups, readily absorbs more water (hydrophilic) compared to commercial CA. Based on the DSC curve, hemicellulose was observed to degrade at a lower temperature of around 170 °C), compared to cellulose, which degrades at a higher temperature of around 250 °C (Huang et al., 2021). The cellulose acetate formed from the esterification of hemp fiber (HCFA) was observed to have a T_g of 134.2 °C which is close to the observed T_s of 131.8 °C.

The T_g is the temperature at which a material experiences changes from a higher crystalline state to an amorphous state and is related to material strength. For amorphous and semi-crystalline materials like cellulose acetate, T_s is usually associated with its glass transition temperature (T_g), which is around 150 – 200 °C depending on the degree of substitution (DS) and if plasticizers are present. (Erdmann et al., 2021). This means that the crystalline portion of cellulosic acetate microfibrils imparted rigidity at

temperatures lower than the T_g and T_s. At elevated temperatures higher than the reported T_g and T_s, the degradation of the crystalline structure led to the formation of an amorphous state, which was softer and less tough compared to the original structure (Filho et al., 2005). It is important to note that the T_g of pure dry cellulose (220 - 250 °C) is higher than that of cellulose esters because of stronger hydrogen bonds between the hydroxyl bonds along the cellulose chain leading to higher crystallinity index (66%) and overall rigidity (Szcześniak et al., 2008). Whereas T_s refers to the point at which a material begins to soften and exhibit deformation and dimensional changes, The melting temperature (T_m) on the other hand, refers to the point at which the material transitions from a solid to a liquid phase. Unlike softening, melting involves the disruption of the crystalline regions of materials into a liquid phase. Since cellulose acetate is mostly amorphous, the observed melting behavior was less distinct compared to crystalline materials.

From TMA data, the commercial CA and HFCA afforded T_m values of 228.2 °C and 220.9 °C, respectively, while DSC data shows T_m values of 222.8 °C and 206.7 °C, respectively. The lower T_m value obtained for HFCA was due to the softening of the hemicellulose moiety which is not present in commercial CA. In simple terms, the softening temperature (T_s) marks the onset of flexibility and deformation, while the melting temperature (T_m) represents complete liquefaction. Both are critical for industrial processing and application design, but they serve different purposes in terms of thermomechanical behavior. In the fiber and textile industries, heat-setting is an important process occurring near or above the T_s or T_g to help stabilize the fibers. Materials used below their T_g tend to maintain their rigidity (e.g., apparel containing polyethylene terephthalate) and elastomers perform well above their T_g to impart flexibility. Meanwhile, T_m is usually used for molding, reshaping, or extruding thermoplastics like polyester. For cellulose and cellulose acetate-based fibers, decomposition starts well before melting, so thermal limitations set for product development are defined by their degradation temperatures rather than T_m. The DS was determined by acid-base titration. DS refers to the average number of -OH groups on each cellulosic anhydroglucose unit replaced by acetyl groups, with a maximum value of 3. The amount of acetyl in terms of % acetyl was calculated through acid-base neutralization based on known volumes and concentrations of alkali (NaOH) titrated with known concentrations of acid (HCl). The partial acidity produced reacted with excess NaOH and the difference between the HCl and NaOH volumes was due to the acidity of the acetic acid produced when NaOH was initially added (alkali hydrolysis using ethanol and heat). There was an observed difference between the calculated % acetyl and DS, as summarized in Table 2. The values obtained for the HFCA were considerably higher than the values calculated for the commercial CA. This was due to partial hydrolysis of the hemp fibers after delignification. Portions of the hemicellulose moiety were still present in the

delignified hemp fiber, thus there were more available free hydroxyl groups present for esterification to occur.

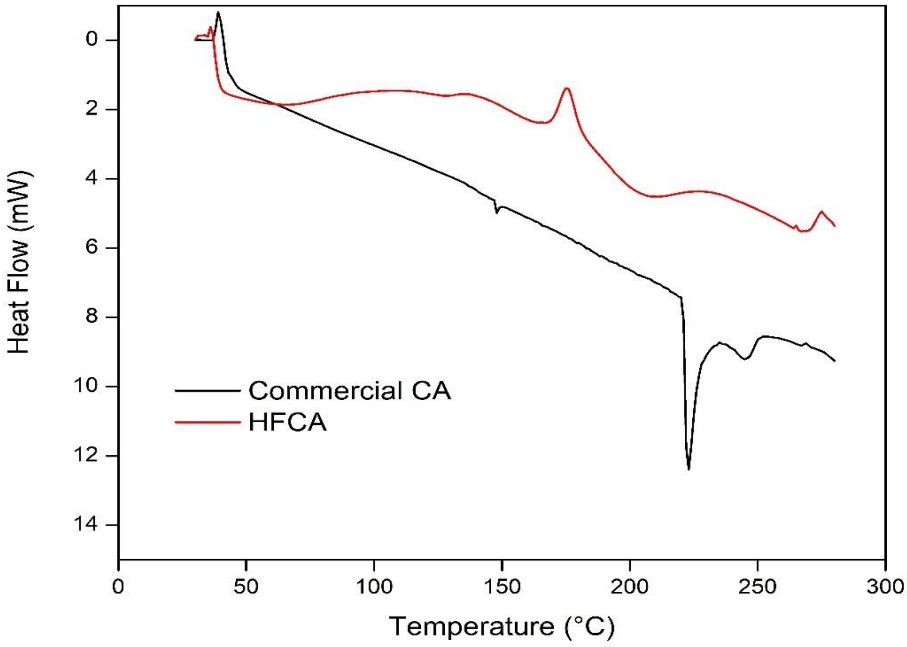

Figure 4. Differential Scanning Calorimetry (DSC) thermogram of commercial CA and HFCA.

Table 2. Calculated % Acetyl, DS, and % Yield values for commercial CA and HFCA (This study) compared with literature values of various natural biomass/fibers.

Sample	Acetyl (%)	DS	Yield (%)	Reference(s)
Commercial CA	40.5	2.5	-	This study
HFCA	47.9	3.4	128.1	This study
Palm fruit CA	40.1	-	156.2	Alim Bahmid et al., 2013
Cotton fiber CA	-	2.9	112.2	Hindi & Abohassan, 2015
Corn cob CA	-	2.7	160.0	Araújo et al., 2020

The DS of CA significantly affects its thermomechanical and physicochemical properties. The T_g of CA decreases as the DS increases mainly due to the reduction in intermolecular hydrogen bonds between the cellulosic chains that hold the cellulose microfibrils. An increase in DS also increases the free volume caused by acetylation. Cellulose acetate with highly substituted acetyl groups (DS = 2.92) exhibits a T_g of ~250 °C, while lower DS results in higher T_g (Kamide & Saito, 1985). On the other hand, T_m increases with DS because a higher amount of acetyl groups enhances the thermal stability of CA because of reduced crystallinity. Also, a higher DS value leads to decreased stiffness and tensile strength but increased flexibility while a lower DS value results in stronger intermolecular interactions, improving mechanical strength (Yadollahi et al., 2019).

Conclusion

Hemp fiber was delignified and esterified to produce hemp fiber cellulose acetate (HFCA). A gain in sample mass (1.1 g) and an increase in % yield (128.1%) was observed due to the substitution of hydroxyl groups present in the cellulose chains of the delignified hemp fiber with heavier acetyl groups. Confirmatory techniques were employed to determine the degree of acetate substitution (DS) by titration, to verify the transformations of functional groups along the process of converting original hemp fiber to hemp fiber cellulose acetate (HFCA) by FTIR, and lastly to determine the changes in dimensional stability and rigidity by TMA and DSC analysis.

Titration yielded 47.9% acetyl and a DS of 3.4 for the HFCA sample. The crystallinity of HFCA was lost when the material transformed into its amorphous state (T_g) as the temperature increased. This also corresponds to the loss in dimensional stability as indicated by the softening temperature (T_s) wherein the material undergoes softening and decreased rigidity. The T_g, T_s, T_m, and DS are critical parameters for tailoring and designing suitable cellulose acetate properties for specific applications, such as films, filters, fibers, and textiles. By carefully adjusting and monitoring these parameters, manufacturers can optimize the mechanical performance, thermal properties, and dimensional stability of cellulose and cellulose acetate-based fibers for diverse industrial uses.

Conflict of Interest: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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