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An Environmentally Friendly Solvent for Cellulose Acetate Production: Ethyl Lactate

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Araştırma Makalesi

Abstract − The aim of this study was to investigate the possibilities of using biodegradable ethyl lactate instead of acetic acid, the most preferred solvent in industrial production, during cellulose acetate synthesis under certain conditions. In the study, dissolving pulp fibres, which were activated with water and acetic acid respectively, were dispersed in ethyl lactate after pressing and then subjected to acetylation reaction with acetic anhydride catalysed by sulfuric acid. The properties of acetylated cellulose were determined using X-Ray diffraction analysis, Fourier-transform infrared spectroscopy, Differential Scanning Calorimetry and other chemical analysis methods (viscosity, the percentage of bounded acid, chemical resistance). It was determined that it was possible to produce cellulose acetate with a DS value of 2.79 in ethyl lactate at 40°C using dissolving pulp. Fourier-transform infrared spectroscopy studies revealed a characteristic band broadening in the 1739 cm^{-1} region, indicating the presence of acetyl groups. The results of X-ray diffraction analyses also showed that the crystalline structure of cellulose was completely dispersed and band broadenings on diffractograms occurred. However, the calculation made on X-ray diffractograms also provided interesting findings in terms of crystallite sizes. It was observed that the crystallite sizes of the acetates were higher compared to the dissolving pulp. It was determined that the high crystallinity of the samples posed a problem in terms of processing properties such as dissolution. Among the solvents used, only Dimethylsulfoxide was found to have sufficient dissolving power.

Keywords *– Synhthesis of cellulose acetate, Ethyl lactate, Solvent exchange, Fourier-transform infrared spectroscopy, X-Ray diffraction analysis*

Selüloz Asetat Üretimi İçin Çevre Dostu Bir Çözücü Seçeneği: Etil Laktat

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Research Article

Öz − Bu çalışmanın amacı, selüloz asetat sentezi sırasında endüstriyel üretimde en çok tercih edilen çözücü olan asetik asidin yerine biyobozunur etil laktatın kullanım olanaklarını belirli koşullar altında araştırmaktır. Çalışma sürecinde, sırasıyla su ve asetik asit ile ön işlemlere (aktivasyona) uğratılmış çözünür hamur lifleri, preslendikten sonra etil laktat içinde dağıtılmış ve ardından sülfürik asit katalizörlüğünde asetik anhidrit ile asetilasyon reaksiyonuna tabi tutulmuştur. Asetillenmiş selülozun özellikleri X-ışını kırınım analizleri, Fourier-transform kızılötesi spektroskopisi ve diğer kimyasal analiz yöntemleri (viskozite, bağlı asit yüzdesi) kullanılarak belirlenmiştir. Çözünür hamuru kullanılarak 40°C'de etil laktat içinde 2,79 DS değerine sahip selüloz asetat üretmenin mümkün olduğu belirlenmiştir. Fourier-transform kızılötesi spektroskopisi çalışmaları, asetil gruplarının varlığını gösteren 1739 cm^{-1} bölgesinde karakteristik bir bant genişlemesi ortaya çıkarmıştır. X-ışını kırınım analizlerinin sonuçları da selülozun kristal yapısının tamamen dağıldığını ve difraktogramlarda bant genişlemelerinin meydana geldiğini göstermiştir. Bununla birlikte, X-ışını difraktogramları üzerinde yapılan hesaplama kristalit boyutları açısından da ilginç bulgular sağlamıştır. Asetatların kristalit boyutlarının çözünür hamura kıyasla daha yüksek olduğu görülmüştür. Numunelerin yüksek kristalinitesinin çözünme gibi işleme özellikleri açısından bir sorun teşkil ettiği belirlenmiştir. Kullanılan çözücüler arasında yalnızca Dimetilsülfoksitin yeterli çözme gücüne sahip olduğu görülmüştür.

Anahtar Kelimeler − *Selüloz asetat sentezi, Etil laktat, Çözücü değişimi, Fourier dönüşümü kızılötesi spektroskopisi, X-Işını kırınım analizi*

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1. Introduction

Cellulose, which is one of the most abundant and sustainable polymers in nature and consists of D-glucose units linked by β-1,4 bonds, is seen as an industrial alternative to petroleum-based materials in many fields after derivatization. Under the subject of esters, there are two types of cellulose derivatives: organic acid esters and inorganic acid esters. Among organic acid esters, cellulose acetate is high in terms of its significance to the industrial market. Its versatility has led to it preferred in many industries, including the textile sector, film and membrane technologies, medicinal applications, injection moulding of plastics, and packaging materials.

There are two primary approaches to acetylation in production: homogeneous and heterogeneous processes. Researchers such as Liebert (2010) states that an innovative method for homogenous acetylation process includes first dissolving cellulose in expensive solvents such dimethyl acetamide-lithium chloride. In most cases, studies conducted in a controlled environment would prefer this kind of acetylation. Many other solvent systems used to dissolve cellulose are available in the literature, but the problem is the same: cost effectiveness. The employment of easily available and cheaper solvents is a hallmark of heterogeneous acetylation process, such as fibrous acetylation process and solution acetylation process. Toluene and benzene are solvents that make cellulose and cellulose acetates insoluble in fibrous acetylation, whereas acetic acid and methylene chloride dissolve reaction products in solution acetylation (Balser et al., 2000; Steinmeier, 2004).

Product quality, reaction efficiency, and environmental issues are greatly affected by decisions made about acetylation processes and solvents. Because of its low cost, acetic acid is preferred for use in solution acetylation (industrial) processes (Mark, 2004). However, problems such as reducing the crystallinity and chain length of the product due to the acidic structure of the process, requiring additional steps to remove residual acetic acid in the product, and requiring additional investments for the recovery of the acid (Klemm et al., 1998; Steinmeier, 2004) cause alternatives to be sought for the solvent. In addition, there are environmental issues with the carbon footprint of producing acetic acid, which ranges from 1.3921 to 1.8746 kg CO_2-eq/kg (Medrano-García et al., 2019; Merli et al., 2021).

Ethyl lactate, with its eco-friendly origins and sustainable production from biomass-derived lactic acid and ethyl alcohol, emerges as a compelling alternative. Aligned with green chemistry principles, ethyl lactate's renewable nature and environmentally friendly production (Pereira et al., 2011) position it as a sustainable choice for cellulose acetate synthesis.

Within limits of the available experimental scope, the study investigates the potential of ethyl lactate in cellulose acetate synthesis studies using acetic anhydride as the acetyl donor and different concentrations of sulfuric acid as the catalyst. The effects of reaction temperature were also investigated. Bound acetic acid, degree of substitution (DS), viscosity, and chemical resistance are some of the experimental characteristics described in the study. The structural and thermal characteristics are revealed by comprehensive characterization utilizing XRD, FTIR, and DSC. This study contributes to our knowledge of cellulose acetylation and draws attention to the unique benefits of ethyl lactate in the synthesis of sustainable and efficient cellulose acetate.

2. Materials and Methods

2.1. Materials

Eucalyptus dissolving pulp supplied by Celltech S.L.U. (Spain) was upgrade to acetate grade level by cold alkali extraction process (10% NaOH solution at 20°C for one hour). The properties of pulp before and after the extraction are given in Table 1. The standards used to determine the properties of the pulp are also summarized in the same table. All chemicals were purchased from Merck KGaA and used without any additional purification.

Table 1
Some properties of cellulose before and after alkaline extraction

Condition	Pulp Viscosity ($cm^3.g^{-1}$) [1]	Kappa Number [2]	Alpha-cellulose (%) [3]	Alkaline solubility [4]			
				S_{10}	R_{10}	S_{18}	R_{18}
Before	478.5	1.00	88.7	10.1	88.5	2.9	92.2
After	522.2	0.97	95.7	4.8	93.0	1.3	95.4

The properties of the pulps determined by following standards; [1]: TAPPI T 230 om-08; [2]: TAPPI T 236 om-13; [3]: TAPPI T203 cm99; [4]: TAPPI T235 cm-00; S_{10} and S_{18}: Soluble portion (%) of pulp in 10% and 18% NaOH; R_{10} and R_{18}: Residual portion (%) of pulp in 10% and 18% NaOH

2.2. Methods

2.2.1. The Synthesis of Cellulose Acetates

Activation of dissolving pulp. To ensure the accessibility of all hydroxyl (OH^-) groups, a one-step deionized water activation followed by two steps of acetic acid activation was applied to the dissolving pulp. Initially, 10 grams of the cold alkaline-extracted dissolving pulp (air-dried) were dispersed in 500 ml of water with the aid of a mechanical stirrer (at 500 rpm) at ambient temperature for 10 minutes. Subsequently, the water in the pulp suspension was eliminated using a Büchner funnel and vacuum flask. In the second activation step, the fibers were dispersed in acetic acid (analytical grade) with the aid of a mechanical stirrer (at 500 rpm) for further activation and to prevent water ingress into the acetylation reactor. The process with acetic acid was repeated twice, and the acid was removed again with the assistance of a Büchner funnel and vacuum flask after each activation step.

Acetylation of dissolving pulp. Following the activation step, in a glass Erlenmeyer flask, the cellulosic fibers were dispersed in a mixture of ethyl lactate (50 ml, solvent) and sulfuric acid (catalyst) until a homogeneous fiber suspension was achieved. The suspension temperature was adjusted to the reaction temperature on a hot plate with a magnetic stirrer (at 500 rpm), and 50 ml of acetylation agent (acetic anhydride) was introduced into the reactor to initiate acetylation. The effects of only two parameters, the reaction temperature (at 20 or 40°C) and catalyst amount (0.1, 0.25, 0.5 or 1.00 ml), were investigated in the implementation of the acetylation process. The reaction time was 180 minutes.

Precipitation of acetylated cellulose. At the end of the reaction, using a separating funnel, the acetate dope was gradually introduced into a 2000 ml of a brine solution prepared with 10 grams of potassium carbonate to stop acetylation reaction and precipitate the acetate particles. The precipitated particles were filtered using a sieve, washed thoroughly with tap water, and allowed to dry at room temperature.

2.2.2. Characterization of Cellulose Acetates

Acetylation degree, viscosity, chemical resistance, structural properties by X-Ray diffractometer and Fourier-transform infrared spectrometer and thermal behaviors by Differential Scanning Calorimeter were studied.

Acetylation Degree. The bounded acetic acid percentage of cellulose acetates (CAs) was determined using the Heterogeneous Saponification Method in accordance with the ASTM D 871-96 standard. In this method, acetylated particles (o.d., 0.5 g) are heated in 75% ethyl alcohol solution at 50-60°C for 30 min. At the end of the time, NaOH solution (0.5 N, 40 ml) was added to flask and the mixture was kept at the same temperature for 15 minutes. The samples are then left at room temperature for 48-72 hours depending on the estimated acetyl percentage of the sample. At the end of the period, the sample is titrated with HCl (0.5 N) solution. After colour transformation, additional HCl (0.5 N, 1.00 ml) is added to the flask and left at room temperature overnight to allow the NaOH to diffuse through the regenerated cellulose. Titration is then continued using HCl (0.5 N) solution until colour stabilization is achieved. The bounded acetic acid percentage of the sample is determined using the following equation:

$$\text{PAC, \%}=[(D-C)Na+(A-B)Nb]\times 6.005/W \tag{2.1}$$

Where, A: the volume (ml) of NaOH solution used for sample titration, B: the volume (ml) of NaOH solution used for blank titration, C: the volume (ml) of HCl solution used for sample titration, D: the volume (ml) of HCl solution used for blank titration, Na: the molar concentration of the HCl solution for titration, Nb: the molar concentration of the NaOH solution for titration, 6.005: a constant related to the molecular weight of acetic acid, W: the sample weight (g).

The following equation was used to determine the degree of substitution (Fan et al., 2009).

Degree of substitution, DS= [(162xAcetic acid content) / (6000-(42xAcetic acid content))]

Where, DS is degree of substitution, 162 g/mol is related to average molecular weight of anyhdroglucose, 6000 is related to the molecular weight of the acetic acid.

Viscosity. For the viscosity measurements conducted within the scope of the study, the method outlined by Buchanan et al. (1991) was employed. In accordance with this method, acetate solutions were prepared by dissolving 0.25 g of cellulose acetate sample in 100 ml of DMSO. Viscometry measurements of the solutions, which were filtered if necessary, were conducted using an Ubbelohde viscometer in a water bath (Schott Gerate, 20000 ml) with the temperature set at 25℃. Viscosity calculations were performed based on the measured flow times of the solutions, employing the following equations:

$$\eta_{REL} = T_2/T_1 \tag{2.2}$$

$$\eta_{SP} = \eta_{REL} - 1 \tag{2.3}$$

$$[\eta] = (2 \times (\eta_{SP} - \ln \eta_{REL}))^{1/2}/C \tag{2.4}$$

Where, η_{REL}: relative viscosity, η_{SP}: specific viscosity, $[\eta]$: intrinsic viscosity, C: concentration of acetate solution (g/ml), T_2: flow time of Cellulose acetate/dimethylsulfoxide solution (sec.), T_1: flow time of dimethylsulfoxide (sec.).

Chemical Resistance. Chemical resistances were assessed utilizing the method described in (Elidrissi et al. 2012). Approximately 0.1 g of acetylated particles were immersed overnight in 3 ml of specific solvents, including toluene, chloroform, tetrahydrofuran, dioxin, diethyl ether, methyl ethyl ketone, cyclohexane, aniline, dimethyl formamide, DMSO (Dimethyl sulphoxide), methanol, and ethanol. Following the period, the response of the samples to the chemicals was observed, and images were captured using a camera.

Molecular Structure. Prior to analyses, dissolving pulp and acetylated particles were ground in a Wiley mill and the particles remaining on a 40-mesh sieve were used for analyses.

A PerkinElmer Spotlight 400 FTIR ATR spectrophotometer (USA) was employed to ascertain and confirm the molecular structure, conformation, and presence of functional groups. Acetylated particles possessing suitable characteristics were prepared using the KBr-disk method for measurements. All FTIR spectra were collected in the range of 4000 cm^{-1} to 500 cm^{-1} with a spectrum resolution of 4 cm^{-1}.

XRD analysis was employed as another technique to elucidate the molecular structure. Structural changes were examined using a Rigaku Ultima-IV X-ray Diffractometer (Ni-filtered Cu-Kα, $\lambda = 0.154$ nm) at 40 kV and 300 mA, with a scanning speed of 1° min^{-1} and a scanning angle range of 5–50. The operating voltage and current were set at 40 kV and 30 mA, respectively. The crystallinity index (CrI) was calculated using the following equation (Segal et al., 1959).

$$CrI = [(I_{002} - I_{am}) / I_{002}] * 100 \tag{2.5}$$

Where, CrI is the degree of crystallinity, I_{002} is the maximum intensity of the (002) lattice diffraction and I_{am} is the intensity diffraction at 18° 2θ degrees.

Thermal Behaviors. A Netzsch DSC 200F3 instrument (Netzsch Group, Germany) was utilized to investigate the thermal behaviors of cellulose-based polymers, including decomposition, crystallization, glass transition, and melting. Prior to analysis, dissolving pulp and acetylated particles were ground in a Wiley mill, and the particles remaining on a 40-mesh sieve were used for the analyses. The tests were conducted at a heating rate of 10˚C.min^{-1} heating rate under nitrogen flow (30 mL.min^{-1}) from 20 to 500 ˚C.

3. Results and Discussion

One of the most crucial factors influencing all behaviors of cellulose derivatives is the quantity of substituents corresponding to each glucose monomer. Indeed, the quantity of substituents shows a direct influence on the structural, thermal, and rheological properties of the polymer. Furthermore, the distribution of substituents along the polymer chain also significantly impacts the aforementioned properties, although it has not been scrutinized in the scope of this study. In Table 2, the percentages of bounded acetic acid, along with calculated DS values and the results of viscosity measurements are presented.

Table 2. Some chemical and rheological properties of cellulose acetate samples synthesized under the solvent effect of ethyl lactate.

Reaction Temperature (˚C)	Catalyst amount (ml)	Sample Code	Acetic acid percentage (%)	DS	Viscosity η_{REL}	η_{SP}	[η]	CRI (%)	C_{002} (nm)
20	0.10	1EL20S010	43.075	1.67	1.15	0.15	55.5	27.9	2.95
	0.25	1EL20S025	40.690	1.54	1.09	0.09	34.3	18.9	3.78
	0.50	1EL20S050	45.333	1.79	1.07	0.07	27.8	12.8	3.60
	1.00	1EL20S100	49.842	2.07	1.03	0.03	11.6	4.2	3.30
40	0.10	1EL40S010	32.464	1.13	1.10	0.10	36.5	52.2	4.51
	0.25	1EL40S025	59.989	2.79	1.05	0.05	18.7	-	-
	0.50	1EL40S050	41.555	1.58	1.12	0.12	44.3	28.7	2.90
	1.00	1EL40S100	31.177	1.36	1.06	0.06	20.9	20.1	3.5
Dissolving Pulp	-	-	-	-	-	-	-	68.9	4.15

Acetylation Degree and Viscosity

Upon examining Table 2, it was observed that cellulose acetate can be successfully synthesized through the utilization of ethyl lactate as a solvent. The DS values of the resulting cellulose acetates range from 1.13 to 2.79, with the highest value observed in the sample labeled 1EL40S025. As detailed in subsequent sections, the finding of successful acetylation is substantiated by thorough analyses conducted using spectroscopy and diffractometer devices. Notably, in syntheses carried out at room temperature, an increase in the catalyst amount positively influenced DS, while an elevation in temperature led to more unstable results. The critical role of the catalyst quantity in influencing the equilibrium between acetylation and cellulose degradation events is well established (Bhatti & Howard, 1976; Steinmeier, 2004). Conversely, intrinsic viscosity values demonstrated a consistent decrease with an increase in the catalyst amount, highlighting an inverse relationship with DS values. This decline in intrinsic viscosity is attributed to the heightened acidity of the reaction medium, resulting in a reduction in the polymer's molecular weight. Furthermore, it is suggested that the quantity and distribution of acetyl groups along the polymer also impact solubility and, consequently, viscosity.

Chemical resistance

It was observed in Figure 1 that the solvents used to assess chemical resistance properties had a limited dissolution effect on cellulose acetates synthesized for similar reasons. Specifically, only DMSO exhibited complete dissolution, while solvents such as Dimethylformamide, Formic acid, and Aniline caused a swelling effect on the samples. No noticeable impact was observed in other solvents. The solubility of cellulose acetate is influenced by various factors, including its chemical composition (degree of substitution, distribution of substituents, hemicellulose content), physical structure (particle size), polarity, molecular mass distribution, and morphological characteristics. Additionally, the type, polarity, and molecular size of the solvent play a crucial role (Pintaric et al., 2000; Shaikh et al., 2009).

The dependence of cellulose acetate solubility on its degree of substitution necessitates a careful selection of solvents for dissolution. Heinze and Liebert (2004), in their comprehensive review, emphasized that cellulose triacetate with a DP value of approximately 300 can be effectively dissolved in dichloromethane, chloroform, chlorinated hydrocarbons, formic acid, acetic acid, aniline, and pyridine. This insight underscores the importance of tailoring solvent choices to the specific characteristics of cellulose acetate, particularly its degree of substitution, to achieve optimal solubility and dissolution outcomes.

Molecular structure

Fourier Transform Infrared Spectroscopy (FT-IR) stands out as a highly valuable analytical technique for identifying functional groups through the measurement of molecular vibrations. Its exceptional molar absorption capacity and the capability to detect carbonyl groups, such as ester groups, even at minimal concentrations make it a preferred method in research. Consequently, numerous researchers have employed FT-IR for the characterization of acetylation in both wood and cellulose (Hurtubise, 1962; Sassi and Chanzy, 1995; Klemm et al., 1998; Popescu et al., 2012).

In the FT-IR spectra of unacetylated and acetylated dissolving pulps (Figure 2), the "fingerprint" region shows significant differences. Upon analyzing the FT-IR spectra, it is well-established that the acetyl/carbonyl groups present in the main chain of cellulose manifest an expansion in the 1720-1760 cm^{-1} band (Heinze and Liebert, 2004; Heinze et al., 2006; Popescu et al., 2012). The characteristic pattern has also been observed in cellulose acetates synthesized in ethyl lactate for all samples, with a broadening that peaks at the wavelength range of 1735-1740 cm^{-1}, as can be seen in Figure 2. No vibration was observed in this region for unacetylated dissolving pulp. The spectral shift aligns with established literature on cellulose acetylation and provides clear evidence of the successful introduction of acetyl groups into the cellulose structure during the synthesis process in ethyl lactate. The main reason for the non-constant location of acetyl groups in FT-IR spectra can be attributed to the variations in acetylation conditions. The reaction parameters applied during the acetylation process, such as the amount of catalyst, temperature etc., can affect the way acetyl groups bound to and the amount of the cellulose molecule. These variations may affect the binding positions of acetyl groups to the cellulose molecule by affecting the intensity, position, and width of the peaks in the FT-IR spectra.

Another evidence of acetylation is the bands appearing in the spectrum of dissolving pulp in the 1200 and 1400 cm^{-1} range (Pethrick and Wilson, 2013, Zhang et al., 2013). The bands around 1240-1280 cm^{-1} are associated with the stretching vibration of C-O bonds. In acetylated cellulose, these peaks are often attributed to the C-O stretching in acetyl groups. Furthermore, the presence of methyl ($-CH_3$) groups in the acetyl groups leads to a characteristic deformation vibration, typically observed around 1375 cm^{-1}.

Figure 1. The photographs showing the chemical resistance of cellulose acetate samples, synthesised under the solvent effect of ethyl lactate, in some solvents (Abbreviations, DMSO: Dimethyl sulfoxide, FA: Formic acid, DMF: Dimethylformamide, ANI: Anillin, TOL: Toluene, THF: Tetrahydrofuran, DIO: Dioxane, DCM: Dichloromethane, ACE: Acetone, DEE: Diethyl ether, CHCl3: Chloroform, CH: Cyclohexane, EtOH: Ethyl alcohol, MetOH: Methyl alcohol. The numbers in the pictures, 18: 1EL20S010, 19: 1EL20S025, 20: 1EL20S050, 21: 1EL20S100, 22: 1EL40S010, 23: 1EL40S025, 24: 1EL40S050, 25: 1EL40S100).

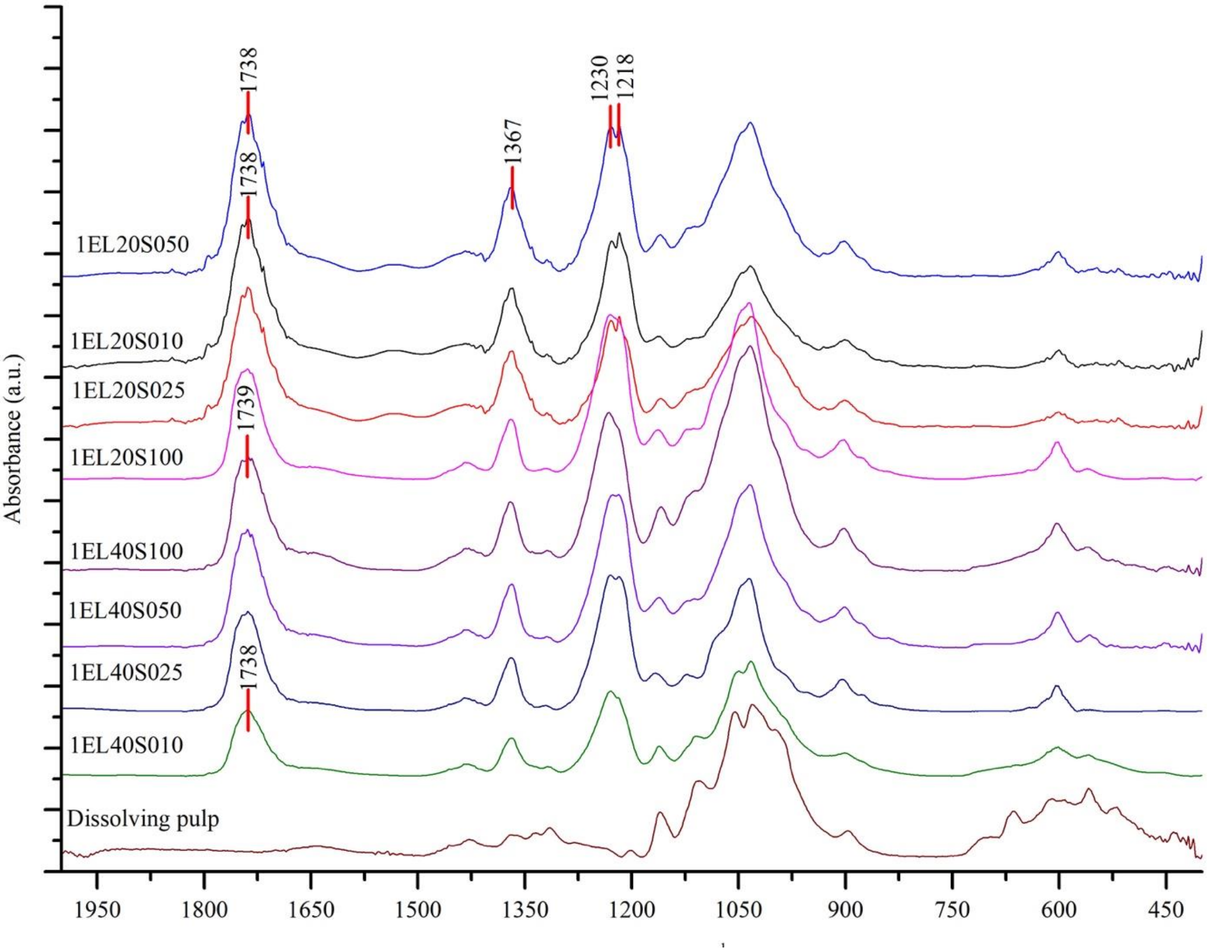

Figure 2. FT-IR spectra in the 2000-400 cm^{-1} of unacetylated dissolving pulp and the samples after acetylation in ethyl lactate

In the 3000-3600 cm^{-1} band range, it is clearly seen that changes occur in the stretching band intensities arising from intra- and inter-molecular H bridges between OH groups (Zhang et al., 2013). The bandwidth of the peaks in the wavelength range of 3000 - 3600 cm^{-1}, which refers to OH groups in the cellulose chain, decreases similar to the previous studies. As seen in Figure 3, the peaks obtained in the wavelength range of 3000 - 3600 cm^{-1} have reached their lowest levels after acetylation reaction. In conclusion, the decrease in peak intensity also indicates a potential modification of OH groups in the cellulose chain during the acetylation process in ethyl lactate.

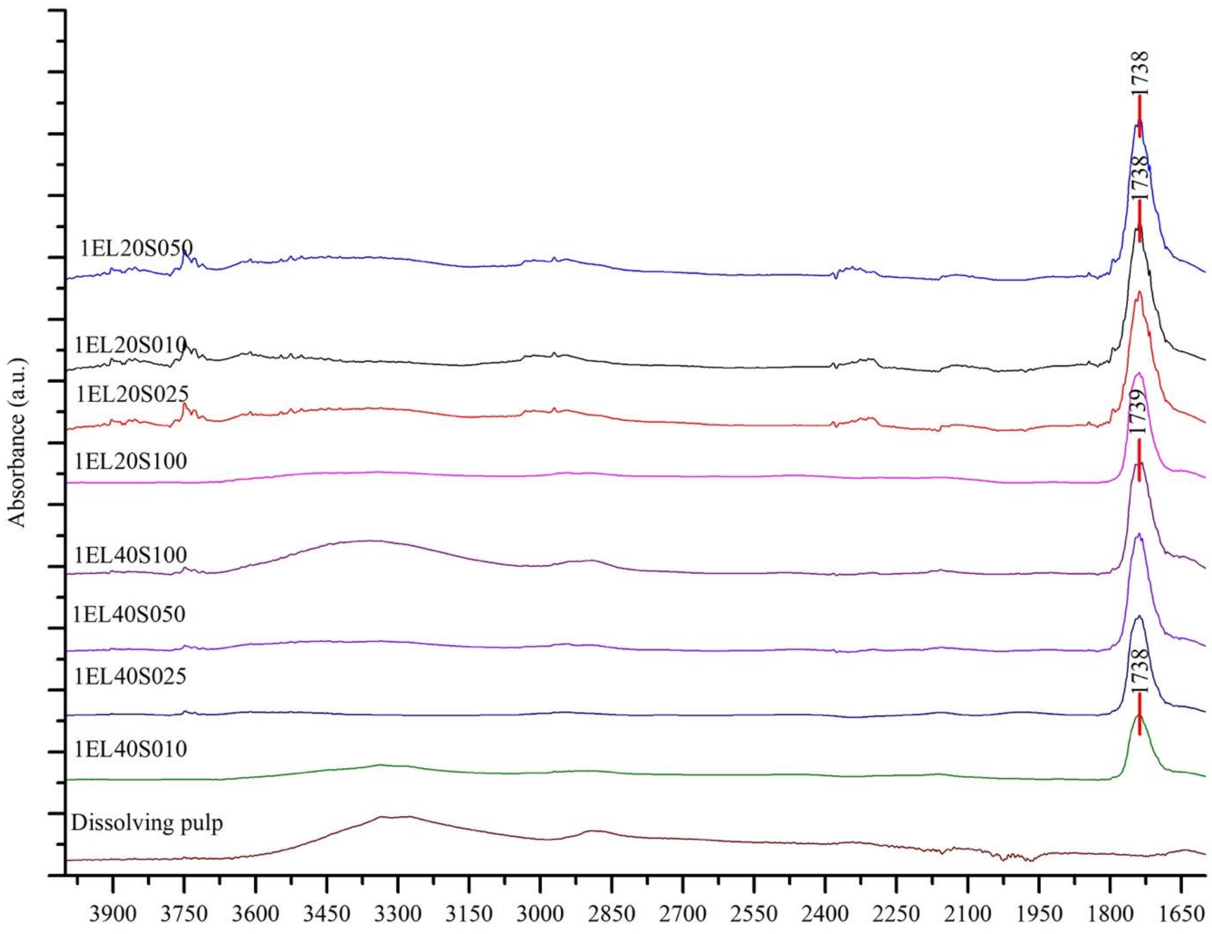

Figure 3. FT-IR spectra in the 2000-400 cm^{-1} of unacetylated dissolving pulp and the samples after acetylation in ethyl lactate

Wide-angle X-ray diffractograms of acetylated and unacetylated samples were thoroughly examined to gain insights into the molecular structure of the materials. The X-ray diffractogram of dissolving pulp exhibited characteristic planes of cellulose, well-documented in the literature (Popescu et al., 2012; Das et al., 2014). A detailed analysis revealed a distinct reduction in reflections at 2θ = 15.0-15.2° (101), 16.7-16.8° ($10\bar{1}$), and 22.5° (002) planes compared to cellulose acetate. Interestingly, these planes, prominently present in the XRD spectrum of dissolving pulp, appeared to diminish following acetylation reactions. A noteworthy feature indicating semi-crystalline acetylated cellulose was the broad reflection observed at 2θ= 8° (Filho et al., 2008; Hu et al., 2011; Popescu et al., 2012), which became apparent in the X-ray diffractogram of dissolving pulp after acetylation. Similarly, diffraction peaks around 10-11° were detected, which were attributed to the crystalline peaks of cellulose acetate II (Das et al., 2014).

The successful acetylation was further evidenced by calculations assessing the degree of crystallinity. Post-acetylation analysis of the diffractograms revealed a decrease in the degree of crystallinity, attributed to the disruption of intermolecular and intramolecular hydrogen bonds in cellulose as hydroxyl groups were replaced with acetyl groups. Barud et al. (2008) reported that during acetylation of cellulose, acetyl groups disrupt the microfibrillar structures of cellulose by changing the spacing of fibrils in the supramolecular structure of cellulose. The steady reduction in crystallinity correlated with an increase in the acetyl group's replacement of hydroxyl groups (Table 2). Additionally, it was observed that the crystallite size, which initially increased at low DS values due to the acidic reaction environment, exhibited a subsequent decrease as the DS value increased. The crystallinity index (CRI) became more apparent with an increasing catalyst quantity, particularly at 40°C. Notably, the CRI, initially determined as 68.9% for the dissolving pulp raw material, exhibited a decrease to 52.2% for sample 1EL40S010. It was observed that the average crystallinity of cellulose acetate samples obtained in the ethyl lactate creates higher results that of previous studies. This heightened crystallinity raises concerns about potential challenges in the processing of cellulose acetates.

For 1EL40S025, the reduction in crystallinity percentage was even more pronounced, indicating the complete dispersion of the crystalline structure. The observed modifications in the degree of substitution (DS) values correlated with similar trends in crystallinity percentages. Likewise, at 20°C, there was a consistent decline in crystallinity percentage with the escalating degree of substitution (DS) values. These findings underscore the intricate relationship between acetylation conditions, DS values, and the resulting crystalline structure, providing valuable insights into the synthesis process.

Thermal behaviors

The thermal analysis results of cellulose acetates synthesized in ethyl lactate at temperatures of 20°C and 40°C are illustrated in Figure 4. The endothermic reaction observed up to 100°C is attributed to the dehydration of the sample (Filho et al, 2008; Cerqueira et al, 2009) but the section is not showed in the figure.

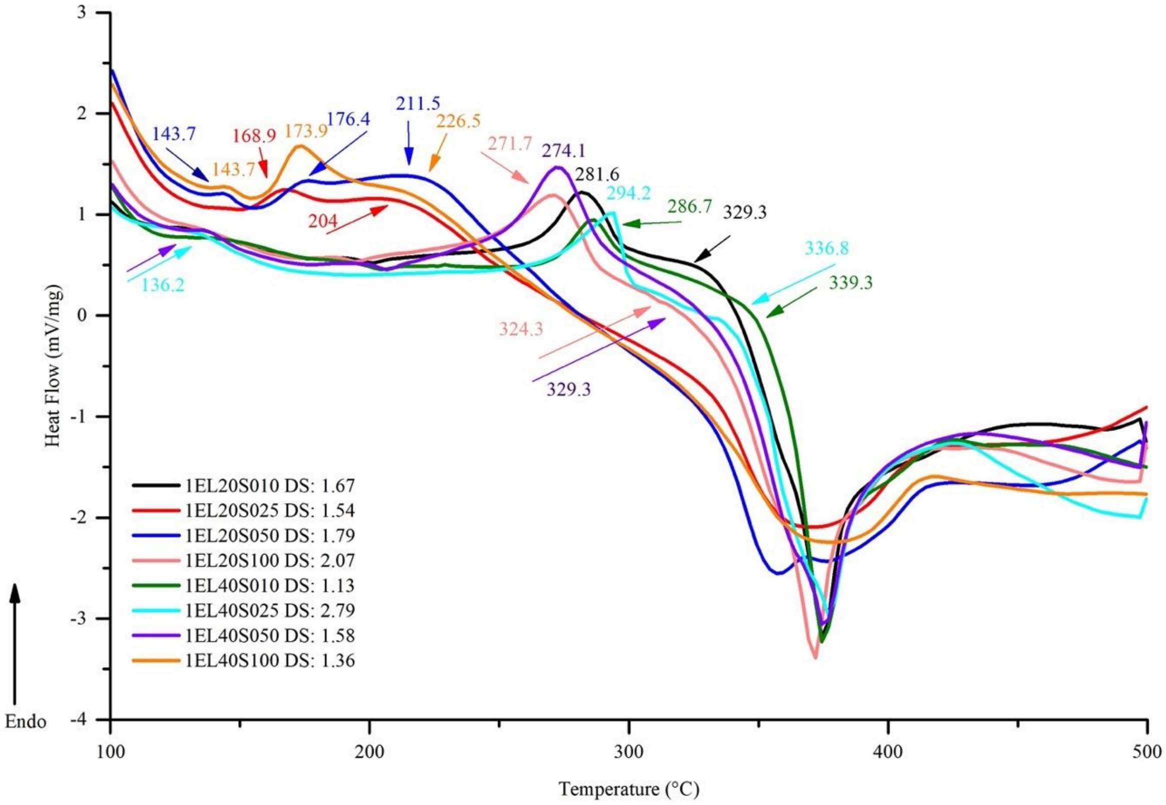

Figure 4. Thermograms of cellulose acetate samples

The initial thermal behavior relates to the glass transition of the sample (Tg), observed consistently across all samples within a specific temperature range. The endothermic behaviors of samples synthesized at both temperatures; it was noted that changes indicative of Tg occurred in the temperature range of 136.0-180°C. It was observed that the Tg of the sample labeled with the 1EL40S025, which has the highest degree of substitution, started earlier than the other samples. With an increase in synthesis temperature to 40°C, the glass transition transformation exhibited an upward trend.

In contrast, Kamide and Saito (1985) conducted an extensive study exploring the effects of total degree of substitution (DS) and average molecular weight on glass transition (Tg), melting point (Tm), and thermal decomposition (Td) values for cellulose acetate samples with varying degrees of substitution and molecular weight distribution. Glass transition temperatures of fractionated cellulose acetate samples (DS=2.92) were found in the range of 181-187°C. Their findings suggested that a decrease in DS value has an increasing effect on the glass transition temperature. Similarly, Zhang et al. (2013) investigated the melting behavior of cellulose acetates with substitution degrees of 1.28, 1.51, and 1.72, finding that this behavior occurred within a wide temperature range of 135-210°C.

The graphical representations reveal that there is no crystallization behavior (Tc) indicating exothermic transformation in both temperature groups, while there is a transformation indicating melting behavior (Tm). However, among the samples synthesized at 40°C, only for 1EL40S100 no melting behavior was recorded. Among the samples synthesized at 20°C, the melting temperature range for 1EL20S010 and 1EL20S100 started around 250°C and the transformation was completed just above 300°C, similar to the samples synthesized at 40°C. As in the Tg; it was observed that the increase in DS value was also effective on the Tm value of the samples, the sample with a DS value of 2.79 started this behavior last and completed the transformation last.

The final observed behavior as the temperature increases is the decomposition temperature (Td) value, signifying the initiation of sample decomposition under temperature influence (Das et al., 2014). It was determined that this exothermic behavior clearly started around 320°C for all samples and showed differences according to the sample structure.

4. Conclusion

The study focuses on the synthesis and characterization of cellulose acetates using ethyl lactate as a solvent under specific conditions.

- The success of the acetylation process was determined based on the chemical properties, and it was confirmed through DS values ranging from 1.13 to 2.79 by saponification method.
- The chemical properties, including DS and intrinsic viscosity, were found to be sensitive to variations in catalyst amount and temperature during synthesis, highlighting the intricate balance in acetylation conditions.
- Solvent resistance exhibited variability, indicating dissolution and partial swelling in some solvents, while others showed no signs of dissolution.
- Fourier Transform Infrared Spectroscopy (FT-IR) revealed the presence of acetyl groups on the cellulose chain at the band of 1735-1740 cm^{-1}, and X-ray diffractograms demonstrated a reduction in crystallinity post-acetylation, with some samples experiencing complete structural disintegration. Further exploration of specific spectral regions in FTIR could provide deeper insights into solvent system influence on cellulose functional groups, contributing to a comprehensive understanding of acetylation-induced structural changes.
- Thermal behavior, encompassing glass transition (Tg), melting (Tm), and decomposition (Td) temperatures, highlighted the significant impact of DS values on material thermal stability.

A complex relationship between chosen synthesis variables, structural, and thermal properties was identified under specific conditions, emphasizing the crucial role of temperature and catalyst amount in tailoring cellulose acetates with desired properties. For next studies, a full factorial design is recommended for a precise assessment of variable effects on acetylation development.

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Author Contributions

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Conflict of Interest

No potential conflict of interest was reported by the authors.

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