Potassium Carbonate as Catalyst for Transesterification of Cellulose in TBAF/DMSO Solvent System Instead of KH$_2$PO$_4$ and Na$_2$HPO$_4$ Salt Mixture

Emir ERİŞİR[1]* , Esat GÜMÜŞKAYA[2]

[1]Sakarya University of Applied Sciences, Pamukova Vocational School, Paper Technology, Serdivan, Sakarya, TÜRKİYE
[2]Karadeniz Technical University Faculty of Forestry, Forest Industry Engineering, Trabzon, TÜRKİYE
*Corresponding Author: emirerisir@subu.edu.tr

Abstract

Aim of study: This study's goal is to evaluate potassium carbonate as a catalyst for the transesterification of cellulose dissolved in TBAF/DMSO and to identify the optimal reaction conditions.

Material and methods: First, a solvent system consisting of 33 g TBAF and 165 g DMSO was prepared for 10 g dissolving pulp in this solvent system for one hour, then the cellulose solution was generated. The catalysts were added to the solution. At reaction temperature, vinyl acetate was added to the solution and the 70-h transesterification process was started. The product was precipitated in ethyl alcohol and washed with water on a sieve, and then dried at room temperature. The effects of changes in catalyst ratio and temperature on bond acetyl groups were investigated by heterogeneous saponification method, FTIR, XRD, DSC, viscosity and solubility test.

Main results: The samples' DS values ranged from 1.39 to 2.37 and using phosphate salt mixture catalyst and increasing the ratio of catalyst increased the DS. FTIR and XRD data revealed that acetylation was effective. DSC thermograms showed a minor endotherm at 283.3-291.2°C, and it was identified as the melting point. With potassium carbonate, the viscosity and the solubility of the products increased.

Highlights: Cellulose in TBAF/DMSO could be acetylated using potassium carbonate as the catalyst. Potassium carbonate's catalyst activity was weak on DS.

Keywords: Cellulose, TBAF/DMSO, Potassium Carbonate, Transesterification, FTIR, XRD, DSC

Selülozun TBAF/DMSO Çözücü Sisteminde KH2PO4 ve Na2HPO4 Tuz Karışımı Yerine Transesterifikasyonunda Katalizör Olarak Potasyum Karbonat

Öz

Çalışmanın amacı: Bu çalışmanın amacı TBAF/DMSO içinde çözünmüş selülozun transesterifikasyonunda potasyum karbonatı katalizör olarak değerlendirmek, uygun reaksiyon koşullarını belirlemektir.

Materyal ve yöntem: 33 gram TBAF ve 165 gram sıvı DMSO'dan oluşan çözücü içerisinde mekanik olarak öğütülmüş yüksek saflık oranına sahip 10 gram çözünür hamur oda sıcaklığında 1 saat süreyle bekletilmiş ve selüloz çözeltisi üretilmiştir. Çözünen selüloza katalizör ilave edilmiş ve yönteme uygunsa ortam sıcaklığı arttırılmıştır. Reaksiyon sıcaklığına ulaşıldığında vinil asetat sisteme ilave edilmiş ve 70 saatlik transesterifikasyon reaksiyonu başlatılmıştır. Sürenin sonunda ürün sırasıyla etil alkol içerisinde çöktürülmüş ve su ile elek üzerinde yıkandıktan sonra, oda sıcaklığında kurutulmuştur. Katalizör oranı ve sıcaklığın değişiminin bağ asetil grupları üzerindeki etkileri heterojen sabunlaştırma yöntemi, FTIR, XRD, DSC, viskozite ve çözünürlük testi ile araştırılmıştır.

Sonuçlar: Örneklerin DS değerlerinin 1.39 ile 2.37 arasında değişmiş ve fosfat tuzu karışımı katalizörünün kullanılması ve katalizör oranının arttırılması ile DS artmıştır. FTIR ve XRD verileri asetilasyonun başarılı bir şekilde gerçekleştiğini göstermiştir. DSC termogramlarında 283.3-291.2°C'de küçük bir endoterm mevcuttur ve bu erime noktası olarak tanımlanmıştır. Potasyum karbonat ile, örneklerin viskoziteleri ve ürün çözünürlüğünün arttığı tespit edilmiştir.

Önemli vurgular: TBAF/DMSO içinde selülozun katalizör olarak potasyum karbonat ile asetilasyonu gerçekleştirilebilir. Potasyum karbonatın katalizör etkisinin DS üzerinde daha az etkili olduğu görülmüştür.

Anahtar Kelimeler: Selüloz, TBAF/DMSO, Potasyum Karbonat, Transesterifikasyon, FTIR, XRD, DSC

Introduction

Chemicals derived from cellulose are very attractive on the market since they may be used either as intermediates or as main components in the manufacture of a wide variety of products. Furthermore, it is one of the most attractive research topics that has recently risen due to the fact that it is obtained from renewable natural resources (Wang et al., 2016). Alternative production methods, the use of different chemicals in existing production processes (such as alternative solvent systems, the functional group donor or the catalysts, the investigation of the feasibility of exploiting new cellulose sources, and so on) are among the new subjects in cellulose chemistry research.

Because of the supramolecular (mainly hydrogen bonding within and between macromolecules) and hydrophobic interactions, cellulose is insoluble in water and common organic solvents (Lindman et al., 2010). The accessibility and reactivity of the OH groups in the biopolymer backbone are restricted in the heterogeneous reaction conditions (Klemm et al., 2005). Cellulose derivatives, however, could be synthesized in either homogeneous or heterogeneous reaction conditions. While heterogeneous reaction conditions are often preferable for industrial derivative synthesis, homogeneous conditions are generally practiced for laboratory-scale cellulose derivative preparation (Heinze et al., 2006a). In heterogeneous systems, the reactions first start in the amorphous regions of the cellulose and then proceed to the crystalline regions. As part of the reactions in a heterogeneous environment, the irregularities appear in the structure of the product produced. The products with characteristics such as unpredictable and often irreproducible DS are obtained (Heinze et al., 2018).

In homogeneous reaction conditions, before the substituents are attached to the biopolymer backbone, cellulose is dissolved by a solvent or an ionic liquid. Heinze and Liebert (2001) categorized cellulose solvents as derivatizing and non-derivating solvents. During the last quarter century, a comprehensive review covering the studies and advances in cellulose solvents was published by Kostag et al. (2019).

Dimethyl sulfoxide containing [TBA]F.$3H_2O$, which dissolves cellulose with a polymerization degree of up to 650 without any pretreatment, is one of the most significant non-derivatizing solvents of cellulose (Heinze et al., 2000; Heinze & Köhler, 2010). The acetylation of cellulose could be performed by transesterification with the aid of preparing cellulose solution in a solvent system (Heinze et al., 2000; Ciacco et al., 2003; Ass et al., 2004; Hussain et al., 2004; Köhler & Heinze, 2007; Nagel & Heinze, 2010). The study of system variables, such as the use of various cellulose sources and acetyl donors, temperature, reaction time, and solvent system ratios, is the dominant focus of studies on the TBAF/DMSO system in the acetylation of cellulose. In the studies, it was found that either no catalyst was employed or just one kind of catalyst was utilized; the effects of other catalysts and the use of various catalyst dosages on the qualities of the final product have not been examined.

The suitability of the TBAF/DMSO solvent combination as a reaction media for homogenous cellulose functionalization was examined by Heinze et al. (2000). It was determined that the product's DS value was increased by the application of a higher molar ratio of vinyl acetate (VA) during the transesterification procedure. They also concluded that the application of potassium phosphate and disodium hydrogen phosphate mixture catalyst (a mixture of KH_2PO_4 and Na_2HPO_4) created a very limited effect on the products.

Even in a very complex structure of wood dust composed of extractives, minerals, lignin, and carbohydrates, the use of catalysts has proven their efficiency on the product. For the acetylation of wood dust, Jebrane et al. (2007) and Jebrane et al. (2011) (by using potassium carbonate and pyridine) and Cetin et al. (2011) (by using potassium acetate, potassium carbonate, and sodium carbonate) studied the impact of these catalysts on the product characteristics. Dicke (2004) also studied the effects of several catalysts on the acetylation of DMSO-dissolved starch. However, the effects of potassium carbonate salt have not been studied in the transesterification of cellulose in TBAF/DMSO.

The study aims to research the effects of two type of catalysts (potassium carbonate and phosphate salt mixture) on the homogenous acetylation of highly pure cellulose with VA following the dissolution of cellulose in TBAF/DMSO. The phosphate salt mixture was selected as the control group. FTIR, XRD, DSC, solubility, DS, viscosity, and other physical, chemical, and thermal characteristics of cellulose acetates produced with both catalysts were investigated.

Material and Method
Materials

Before starting the transesterification procedure, the characteristics of the Eucalyptus low-grade dissolving pulp supplied by Celltech S.L.U. (Spain) were enhanced using a cold alkaline treatment (10% NaOH solution at 20°C for one hour). The characteristics of dissolving pulp and the results of purification are reported in Table 1. The standards used to determine the qualities of pulp were also described in the same table. All chemicals were purchased from Merck KGaA and utilized without any additional purification.

Methods
The Transesterification in TBAF/DMSO

The results of studies about the synthesis of cellulose acetate utilizing the TBAF/DMSO solvent combination have been reported by different researchers. However, in contrast to previous studies, the potassium carbonate catalyst was employed in the transesterification of high-grade cellulose. The high-quality cellulose was dissolved in a TBAF/DMSO solvent mixture to make cellulose acetate. To obtain a clear cellulose solution, firstly, 33 g TBAF salt was combined with 165 g liquid DMSO (Heinze et al., 2000). Then, 10 g (0.098 moles) of mechanically disintegrated high-grade dissolving pulp was added into the solution of TBAF/DMSO. The cellulose was dissolved in 15 minutes at room temperature. The cellulose solution was heated to the reaction temperature, if necessary, and the catalysts were added when the temperature was reached. The catalyst in the transesterification was potassium carbonate or a combination of the phosphate salts, while VA was selected as the acetylating agent.

Table 1. The properties of raw and extracted dissolving pulps

The type of dissolving pulp	Pulp Viscosity[1], $cm^3.g^{-1}$	Kappa Number[2]	Alpha cellulose[3], %	Alkaline solubility[4], %			
				S10	R10	S18	R18
Raw	478.5	1.00	88.7	10.1	88.5	2.9	92.2
Alkaline Extracted(AE)	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 cm-99; 4: TAPPI T235 cm-00; S10 and S18: Soluble portion (%) of pulp in 10% and 18% NaOH; R10 and R18: Residual portion (%) of pulp in 10% and 18% NaOH

Based on the research conducted by Heinze et al. (2000), the phosphate mixture catalyst was prepared as follows: In a container, 33 ml of a 0.2 M solution of potassium dihydrogen phosphate and 67 ml of a 0.2 M solution of disodium hydrogen phosphate were combined. The prepared solution was heated to 105±3°C until all the water evaporated. The completely dehydrated phosphate salt combination was kept in a sealed container. For each experiment, either 10 or 20 mg of the phosphate salt combination was applied. In the systems applied potassium carbonate, the carbonate is introduced straight to the reaction media without any pre-treatment. The catalysts were added to the

system when the cellulose solution reached the temperature of the reaction.

Once the catalyst was completely dissolved in the cellulose solution, 63.77 g of the acetylating agent VA was added, and a 70-hour reaction period was started. After the addition of VA, the colour of the cellulose solution started to darken during the transesterification period, resulting in a dark brown solution at the end of the reaction period. The produced cellulose acetate was poured onto ethyl alcohol and allowed to precipitate following the transesterification process. After sieving, it was rinsed with large amounts of water and allowed to dry at room temperature. The all parameters and results for the transesterification of cellulose in the

TBAF/DMSO solvent system were described
in Table 2.

Table 2. The conditions and results of the transesterification[1] of cellulose dissolved in TBAF/DMSO for 70 h

Reaction Variables	D. Pulp	Phosphate salts mixture catalyzed				Potassium carbonate catalyzed			
		PSM1	PSM2	PSM3	PSM4	PC1	PC2	PC3	PC4
React. Temp. (°C)		20	20	40	40	20	20	40	40
Cat. Amount (mg)		10	20	10	20	10	20	10	20
Properties									
PAC (%)[2]		47.56 (±0.28)	54.39 (±0.14)	50.92 (±0.08)	51.66 (±0.32)	51.02 (±0.88)	51.92 (±0.37)	45.91 (±0.41)	44.76 (±0.10)
DS[3]		1.92	2.37	2.14	2.18	1.75	1.84	1.49	1.39
Viscosity [η] (dl/g)		-[4]	1.76	2.13	1.73	2.24	1.86	-	2.92
Crystallinity (%)	68.9	8.4	5.8	10.2	12.2	4.5	4.2	15.9	15.6
CSize$_{200}$ (nm)	4.15	0.90	0.93	1.50	2.00	1.00	0.90	1.70	1.50
Solvent Type									
Aniline	-	G	-	G	G	G	G	+	+
Acetone	-	Δ	Δ	-	Δ	Δ	Δ	Δ	Δ
Chloroform	-	-	-	-	+	+	+	+	+
Dichloromethane	-	Δ	Δ	Δ	Δ	Δ	Δ	Δ	Δ
Dimethyl sulfoxide	-	G	G	G	G	G	G	G	G
DMF[5]	-	G	G	G	Δ	Δ	Δ	Δ	Δ
Formic acid	-	G	G	Δ	G	+	+	+	+
Cyclohexane	-	-	-	-	-	-	-	-	-
Toluene	-	G	G	G	Δ	Δ	Δ	-	Δ
Tetrahydrofuran	-	-	-	-	-	-	-	-	-
Dioxane	-	Δ	-	Δ	Δ	Δ	Δ	+	+
Diethyl ether	-	-	-	-	-	-	-	-	-
Ethanol	-	-	-	-	-	-	-	-	-
Methanol	-	-	-	-	-	-	-	-	-

(1) Mol acetylation agent per mol anhydroglucose unit was 7.063; (2) Percentage of acetyl content (PAC) was determined according to ASTM D-871; (3) DS, degree of substitution calculated from PAC (%); (4) Not determined; (5) Dimethylformamid; +: Soluble; G : Gelation; Δ : Partially soluble and - : Not soluble

Characterization of Cellulose Acetate Samples
Determination of Bonded Acetic Acid Content and Degree of Substitution

The acetic acid content of cellulose acetates was evaluated using the ASTM D 871-96 standard's Heterogeneous Saponification Method. In a container with a cover, 0.5 g oven-dried cellulose acetate and 40 ml of 75% ethyl alcohol-water were mixed. It was heated in a water bath between 50 and 60°C for 30 minutes. After 30 minutes of heating, 40 ml NaOH solution was added to the mixture, and it was heated for an additional 15 minutes in the bath. The sample was then allowed to rest for 48 or 72 hours, depending on its acetyl concentration. The excess NaOH in the flask was titrated with a 0.5 HCl solution using phenolphthalein as an indicator, and approximately 1 ml of excess HCl solution was added.

The flask was left overnight at room temperature in order to diffuse NaOH from regenerated cellulose.

The equation 1 was used to calculate the percentage of *Bonded Acetic Acid Content (BAC)*.

$$\% = [(D-C) N_a + (A-B) N_b] \times 6.005/W \qquad (1)$$

where; A was volume (mL) of NaOH solution used for sample titration; B was volume (mL) of NaOH solution used for blank titration; C was volume (mL) of HCl solution used for sample titration; D was volume (mL) of HCl solution used for blank titration; N_a was molar concentration of HCl solution for titration, N_b was molar concentration of NaOH solution for titration, 6.005 was related to the molecular

weight of the acetic acid and W was the sample weight in grams.

The equation 2 was used to determine the degree of substitution;

$$DS = [(162 \times BAC\ Content) / (6005 - (BAC \times 42))]\quad (2)$$

where; DS was the degree of substitution, 162 g/mol was related to the average molecular weight of anyhdroglucose, 6005 was related to the molecular weight of the Acetic Acid.

Viscosity

Intrinsic viscosity was measured using an Ubbelohde viscometer by Buchanan et al. (1991). For viscosity measurements, a 20L Schott Gerate bath with temperature control and water circulation was fitted with an Übbelohde-type viscometer. All measurements were conducted at 25 °C at a concentration of 0.25 g cellulose acetate per 100 ml DMSO. Cellulose acetate was initially dissolved in DMSO, and residues were filtered if necessary. The flow time of the cellulose acetate solution was measured and collected data was used in the following equations (Eq. 3):

$$\eta_{REL} = T_2/T_1$$
$$\eta_{SP} = \eta_{REL} - 1 \quad\quad\quad (3)$$
$$[\eta] = (2 \times (\eta_{SP} - \ln \eta_{REL}))^{1/2}/C$$

Where, η_{REL}: Relative viscosity, η_{SP}: Specific viscosity, $[\eta]$: Intrinsic viscosity, C: Concentration of cellulose acetate solution (g/ml), T_2: Flow time of cellulose acetate solution (sec.), T_1: Flow time of dimethylsulfoxide (sec.)

Solubility

A little amount of Wiley-milled cellulose acetate was soaked overnight in 3 ml solvent. The solubility of cellulose acetate was evaluated using toluene, chloroform, tetrahydrofuran, dioxin, diethyl ether, methyl ethyl keton, cyclohexane, aniline, dimethyl form amide, DMSO (Dimethyl sulfone), methanol, and ethanol.

Fourier Transform Infrared Spectroscopy

Cellulose acetates were ground in a Wiley mill in preparation for FTIR spectroscopy analysis. The sample for testing were produced using the KBr-disk technique. All FTIR spectra were obtained with a spectral resolution of 4 cm^{-1} using an FTIR ATR spectrophotometer (PerkinElmer Spotlight 400, USA) across the range of 4000 cm^{-1} to 500 cm^{-1}.

Wide Angle X-ray Diffraction Analysis

In a Wiley mill, dissolving pulp and cellulose acetates were ground to provide ready for XRD analysis. X-ray diffraction analysis was done with a Rigaku Ultima-IV (Ni-filtered Cu-Ka, k = 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 was 40 kV, and the operating current was 30 mA. The equation 4 was used to figure out the crystallinity index (CrI): (French, 2014).

$$CrI = [(I_{200} - I_{am}) / I_{200}] * 100 \quad\quad (4)$$

where CrI is the degree of crystallinity, I_{200} is the maximum intensity of the (200) lattice diffraction and I_{am} is the intensity diffraction at 18° 2θ degrees.

Differential Scanning Calorimetry

The thermal behavior of specimens was studied using a Netzsch DSC 200F3 equipment (Netzsch Group, Germany). From 20 to 500 °C, the tests were conducted at a heating rate of 10 °C.min^{-1} under a nitrogen flow of 30 mL.min^{-1}.

Results and Discussions
The Transesterification of Cellulose in TBAF/DMSO

Dissolution mechanism of cellulose in TBAF/DMSO solvent system is not fully elucidated. Östlund et al. (2009) stated that DMSO, which contains sulfoxide sulfur and sulfoxide oxygen groups, is an important agent for the swelling of cellulose due to its polar and aprotic properties. It is able to penetrate the cellulose fibers and further disrupt the hydrogen bonds and van der Waals interactions. On the other hand, they argued that the fluorine in the structure of TBAF dissolves in DMSO and that after dissolution, the fluorine ion can easily interact with OH and acetal oxygen atoms because it is a very

strong hydrogen bond acceptor; as a result, the highly strong bond structure between the polysaccharide chains is severely damaged. This causes the cellulose fibers to separate into individual chains and dissolve into the solvent. Figure 1 shows one of the possible scenarios for cellulose dissolution in TBAF (Seoud et al. 2013).
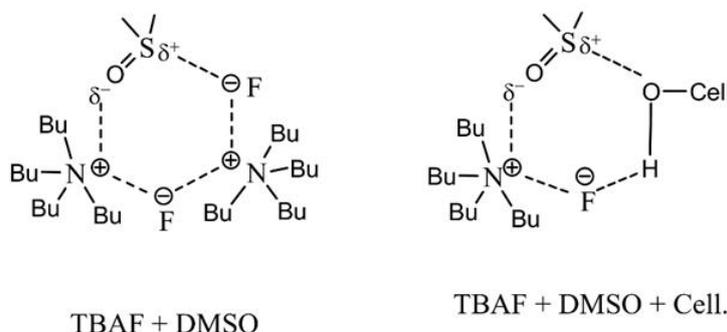

TBAF + DMSO   TBAF + DMSO + Cell.

Figure 1. The possible relationship between cellulose and the TBAF/DMSO solvent system.

Similarly, there is no study in the literature that clearly explains the mechanism of cellulose solution acetylation with vinyl acetate. However, it is believed that transesterification with vinyl acetate occurs as follows. The potassium acetate protonates the hydroxyl groups on the cellulose and the vinyl acetate, increasing their reactivity and facilitating the formation of an ester bond between the cellulose and the vinyl acetate. The cellulose ester intermediate then undergoes a series of elimination and condensation reactions to form the final cellulose acetate product.

Degree of Substitution

In this study, transesterification of cellulose dissolved in TBAF/DMSO was performed using VA as an acetylating agent with two different catalysts. The effects of the change of catalyst ratio and of the temperature on the bond acetyl groups on cellulose backbone which were calculated according to ASTM D 871-96 standard's Heterogeneous Saponification Method and the degree of substitution of cellulose acetate samples were represented in Figure 2.

The DS values, calculated by the saponification method, of the synthesized cellulose acetates were found to change between 1.39 and 2.37. It was revealed that the quantity of bond acetic acid in the sample PC4 was the lowest of all groups. Heinze et al. (2000) found that the DS value of cellulose acetate synthesized by catalyst-free transesterification of VA for 70 h at 40°C was 1.04. On the other hand, using the same quantity of VA and 20 mg of phosphate catalyst, the transesterification resulted in a small increase of DS value to 1.07 at the same reaction conditions. They concluded that the effect of catalyst use was limited but more hydroxyl groups were changed by acetyl groups when more VA was used for transesterification. The moles ratio of the acetyl compound increased from 2.3 to 10, and the DS value increased to 2.72. We obtained DS values of 2.18 for PSM4 and 1.39 for PC4 as a result of transesterification performed under the same conditions which used by Heinze et al. (2000).
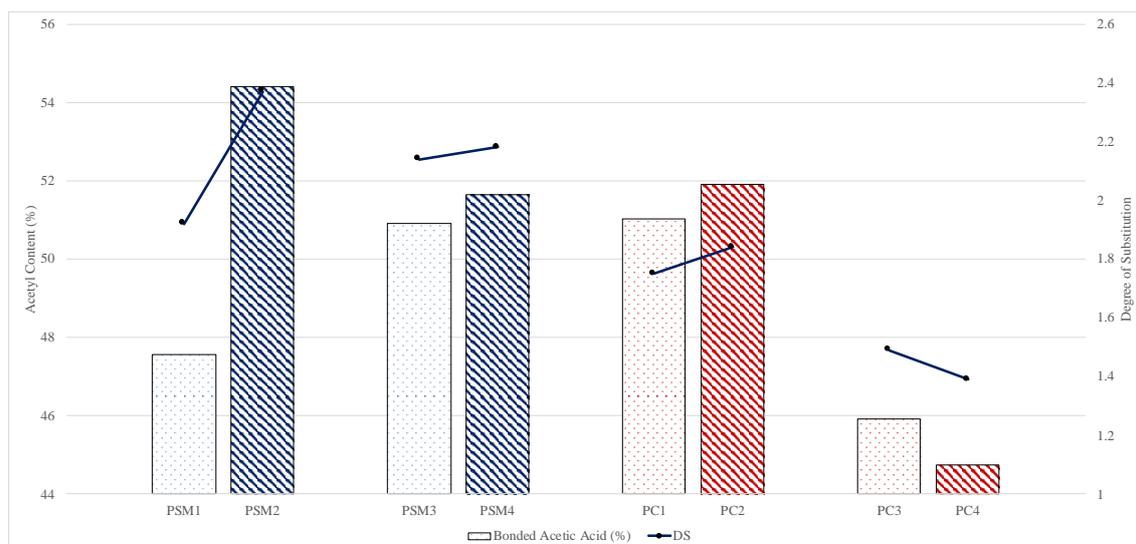
Figure 2. The effects of catalyst ratio and the reaction temperature on the bond acetic acid percentage

Another catalyst-free transesterification conducted by Ciacco et al. (2003), alkali-treated and untreated sisal cellulose was dissolved in a DMSO/TBAF system and acetylated with acetic anhydride for 3 h at 60 °C. They reported that the DS values for the cellulose acetates was between 0.30 and 1.29. They indicated that when the percentage of TBAF employed in the DMSO/TBAF combination was decreased, the DS value was increased. Using the DMSO/TBAF solvent solution, Ass et al. (2004) performed the catalyst-free reaction of cotton linter with various mole ratios of acetic anhydride at 60, 100, or 130 C for 1.5 – 3.0 – 14 and 24 hours. Modifications in reaction parameters such as acetic anhydride ratio, TBAF ratio in the solvent system, time and temperature in catalyst-free transesterification were reported to have effects on DS. Köhler and Heinze (2007) dissolved different types of cellulose (microcrystalline cellulose, spruce wood cellulose powder, cotton linter, bleached cotton fibres) in DMSO/TBAF, followed by catalyst-free transesterification with vinyl acetate at 40°C and 70 h. The highest DS value was determined as "1.25".

At room temperature, the amount of catalyst used in transesterification correlates positively with the amount of acetyl attached to the cellulose backbone. However, for the group of PC3-PC4 (70 h at 40°C), the DS value decreased when the quantity of catalyst was increased. Similarly, Jebrane and Sebe (2007) concluded that the efficiency of VA transesterification increased with the amount of catalyst in the acetylation of wood with VA at the same reaction temperature.

Moreover, the effect of catalyst type on the efficiency of cellulose transesterification by VA was examined. We concluded that systems that used a mixture of phosphate salts (PSM series) yielded higher DS than systems that used potassium carbonate (PC series) as a catalyst. Dicke et al. (2004) investigated the transesterification of starch by VA using a variety of catalysts and found that potassium carbonate with alkaline properties was the most efficient catalyst. Çetin et al. (2011) reported that potassium carbonate was a more effective catalyst in the transesterification of wood with VA, than potassium acetate and sodium carbonate. In briefly, the amount of catalyst improves DS over catalyst-free systems. Vinyl acetate gives equivalent DS values as catalyst-free acetic anhydride in TBAF/DMSO, but it's cheaper, simpler to acquire, and less sensitive to water.

The transesterification with VA was also investigated in terms of temperature. We found that, for both catalysts, increasing transesterification temperature from 20°C to 40°C caused more acetyl groups bonded to the cellulose backbone except PC3-PC4 group.

FTIR

The FTIR spectra of the materials, which can be seen in Figure 3, demonstrate that the transesterification process was carried out effectively. The OH group bands in the range of 3300-3500 cm^{-1} were shown in cellulose to be largely disappeared, and the acetyl group band, which is not present in native cellulose, was observed in the range of 1760 to 1725 cm^{-1} (Yang et al., 2008; Fan et al., 2009; Shaikh et al., 2009; Fan et al., 2010; Meireles et al., 2010; Loo et al., 2012; Popescu et al., 2012). The presence of two characteristic peaks is another evidence that the transesterification of cellulose was achieved. The first was at around 1367 cm^{-1} corresponding to C–O stretching in the acetyl group, while the second was at 1229 cm^{-1} relating to C–H bending in the methyl of the acetyl group. After transesterification with both catalysts, it was determined that the OH groups of the cellulose chains nearly disappeared in the same way, and that the acetyl groups were represented as peaks in the C=O band broadening.
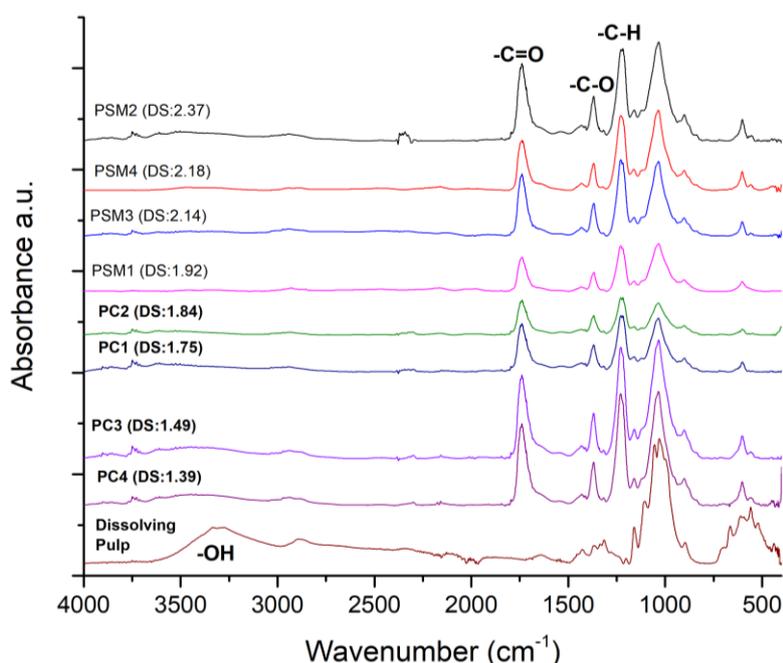

Figure 3. FTIR spectra of cellulose acetates and of dissolving pulp.

XRD and Crystallinity

Figure 4 shows XRD diffractograms obtained for cellulose acetates, produced in TBAF/DMSO with both catalyst at both temperatures, and for dissolving pulp. The 1α and 1β phases of native cellulose are identified by peaks that are located at 15° and 22.5°, respectively (Wada & Okano, 2001; Gümüskaya et al., 2003). CA samples indicating a highly amorphous structure are characterised by the absence or strong reduction of all peaks corresponding to planes (101), (10$\bar{1}$), and (200) in the XRD diffractograms (Ciololcu et al., 2011). On the other hand, it was clearly observed that there is a corresponding change at around 8°, which is the principal characteristic of crystalline acetylated cellulose (Filho et al., 2000; Barud et al., 2008; Ahmad et al., 2020). According to the XRD diffractogram in Figure 3, the stronger reflection (2θ) occurred at 8.5° in samples with a greater DS value. Bendaoud and Chalamet (2014) concluded that initial cellulose acetate (CA) presents a crystalline pattern structure with strong reflection (2θ) located at 8.5°, 10.5°, 13.5°, 17.5° and 23.5°. The semicrystalline region of CA is identified with the diffraction peaks at 8.5° and 10.1° (2°), while the diffraction peak at 17.2° is attributed with the less ordered or amorphous region of CA (Fan et al., 2013). The effects of temperature and catalyst type on the degree of crystallinity and crystallite size were evaluated by calculations using the Segal

method and Scherrer equation. The changes in cellulose's crystal structure following transesterification with both catalysts at 20°C and 40°C in DMSO/TBAF were summarised in Table 2. After the transesterification, it was determined that CrI, which was 68.9 for dissolving pulp, changed from 4.2 to 15.9. According to Hu et al., 2011, cellulose's intermolecular and intramolecular hydrogen bonds are disturbed when hydroxyl groups are replaced by acetyl groups of larger volume. This results in a more amorphous structure. Transesterification at higher temperatures,

using both catalysts, yielded products with better crystallinity because of the elimination of low molecular weight cellulose acetates and celluloses. The PC2 sample has the lowest crystallinity among all other samples. It was also found that the crystallite sizes of cellulose acetates, which were lower than those of dissolving pulp (4.15 nm), changed between 0.90 and 2.00 nm. Glegg et al. (1968) reported that when the quantity of acetyl bonded to the cellulose chain increased, the crystallite length reduced by more than 40% and the width by around 15%.
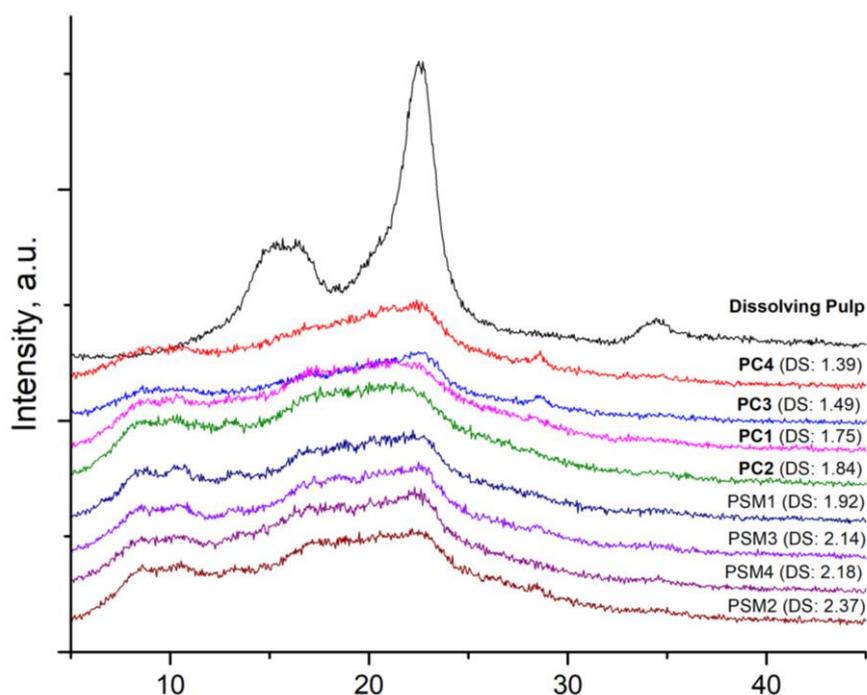

Figure 4. The X-ray diffractograms of cellulose acetates and dissolving pulp.

DSC

The results of thermal analyses conducted on transesterified cellulose samples using a Netzsch DSC instrument are shown in Figure 5. In the sample group using both catalysts, a peak was identified showing an endothermic reaction, indicating that water evaporated first, between 75-125°C (Barud et al., 2008; Cerqueira et al., 2009; Fan et al., 2009; Meireles et al., 2010; Shaikh et al., 2009). All sample groups showed a minor endotherm at 283.3-291.2°C. The endothermic peak in this

location was attributed to the melting temperature by Saka and Ohmae (1996), Tang et al. (1996) and Cerqueira et al. (2009), whereas others attributed it to carbohydrate breakdown (Barud et al., 2008; Meireles et al., 2010). The crystallinity ratios of the samples, in Table 2, represent that the melting temperature could be associated with the region. Over 325°C as expected, a strong exothermic peak represented the thermal degradation of cellulose acetate.
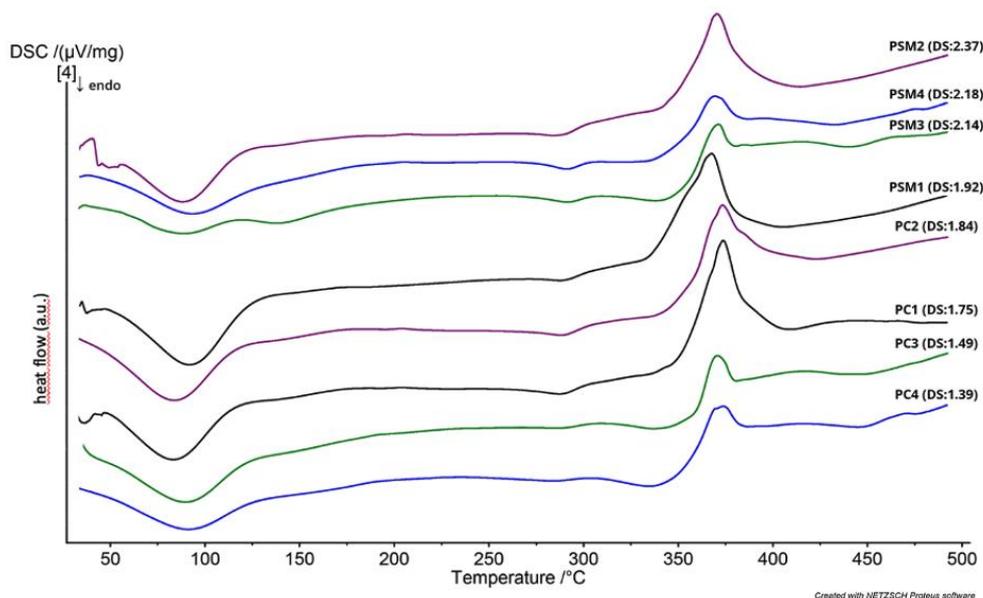
Figure 5. DSC curves for cellulose acetate samples

Viscosity

Cellulose acetate's intrinsic viscosity is highly influenced by structural properties such as DS, the distribution of substituents and the position of substituents and the average length of the cellulose crystallites Glegg et al. (1968). The viscosity values measured for cellulose acetates were summarized in Table 2. Due to the gelation of the polymer in DMSO, it was unable to measure the viscosity of PSM1 and PC3-coded samples.

The intrinsic viscosities seem to be influenced by the type of catalyst. The viscosity measurements ranged between 1.86 and 2.92 for potassium carbonate and between 1.73 and 2.13 for the phosphate salt combination. The results were found to be similar to the study of Shaikh et al. (2009) however, considering that the method used has a lower degradation effect on cellulose compared to previous studies, it can be said that these data are relatively low. Comparing the intrinsic viscosity results of the two catalysts, transesterification with potassium carbonate produced greater DS values. Due to the increase in temperature, it was determined that the viscosity of the transesterification with potassium carbonate increased. The change of reaction temperature could be the cause of the elimination of low molecular weight cellulose acetates and celluloses.

Solubility

It is widely recognized that cellulose has a highly strong hydroxyl bond structure, hence its solubility in common solvents is limited or impossible (Lindman et al., 2010; Ahmad et al., 2020). Therefore, cellulose is transformed by chemical modifications to its ester, ether or etc in order to improve the given features (Heinze et al., 2006b). In the part summarizing the XRD results (Figure 3), it was stated that strong and complicated hydroxyl bond structure of cellulose was distributed (Ahmad et al., 2020) and it is created cellulose acetate with an amorphous structure after the addition of acetyl groups to the cellulose chains (Hu et al., 2011).

The solubility of cellulose acetate varies by DS and the distribution of acetyl groups on the anhyroglucose units (AGU) as well as other physicochemical properties of CA (Kono et al., 2017).

Table 2 presents the solubility of cellulose acetate samples synthesised using phosphate salt and potassium carbonate catalysts in DMSO/TBAF. The samples for both catalysts were sensitive to most of solvents, resulting in either dissolution, gelation, or partial dissolution but they were insensitive to diethyl ether, methanol, ethanol, and tetrahydrofuran.

It was revealed that the samples which was transesterified with potassium carbonate catalyst showed better solubility. The samples in this group showed complete dissolution in

common solvents such as chloroform and formic acid. Potassium carbonate creates a mildly basic environment for organic processes (Kidwai et al., 2013), which can neutralize the acid groups on cellulose and make the cellulose more hydrophilic. Therefore, it may have resulted in higher resolution for samples produced using potassium carbonate.

Another possible explanation for the higher solubility of cellulose acetates produced with potassium carbonate catalysis is that potassium carbonate is more effective in promoting the formation of ester linkages between the cellulose and acetyl groups. Potassium carbonate can act as a nucleophile in the reaction, attacking the carbonyl carbon of the vinyl acetate, which can lead to a higher yield of ester linkages. This can also contribute to the higher solubility of the cellulose acetates produced.

Conclusion

In this paper, cellulose dissolved in TBAF/DMSO was acetylated using VA and two different catalysts. The effects of the change of catalyst ratio and of the temperature on the bond acetyl groups on cellulose backbone was investigated by saponification method, FTIR, XRD, DSC, viscosity and solubility test.

The DS values, calculated by the saponification method, of the synthesized cellulose acetates were found to change between 1.39 and 2.37. In terms of DS, a combination of phosphate salts was found to be more effective than potassium carbonate in the transesterification of cellulose. Moreover, the catalyst ratio is positively correlated with the amount of acetyl groups bonded to the cellulose backbone. Increasing the transesterification temperature from 20°C to 40°C formed more acetyl groups bonded on the cellulose backbone for the combination of phosphate salts.

FTIR spectra and XRD diffractograms also confirmed successful transesterification. In the region of 1760 to 1725 cm^{-1} of the FTIR spectrum, a peak indicating effective acetylation was achieved, while the intensity of the peak indicating OH groups reduced dramatically. After transesterification, it was determined that the CrI and Crystallite size

values identified for native cellulose in XRD diffractograms decreased significantly.

The thermal and physicochemical properties of cellulose acetates were studied by DSC, viscosity measurements and solubility tests. All sample groups displayed a minor endotherm attributed to the melting temperature at 283.3-291.2°C on DSC thermograms. As a result of increasing the temperature, exotherms were observed indicating that the samples started to decompose. It was determined that the viscosity values of the samples increased slightly with the use of potassium carbonate in transesterification. There is no clear relationship for the effects of changes in temperature and catalyst ratio on viscosity. The samples transesterified with potassium carbonate catalyst showed better solubility.

Ethics Committee Approval

Due to the scope of the study, there was no need for an ethics committee permission document.

Peer-review

Externally peer-reviewed.

Author Contributions

Conceptualization: E.E., E.G.; Investigation: E.E., E.G.; Material and Methodology: E.E., E.G.; Supervision: E.G.; Visualization: E.E.; Writing-Original Draft: E.E..; Writing-review & Editing: E.E., E.G.; Other: All authors have read and agreed to the published version of manuscript.

Conflict of Interest

The authors have no conflicts of interest to declare.

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