

Synthesis of Hybrid Cellulose Acetate Membranes and Application of the Flynn-Wall-Ozawa Isoconversional Method[☆]

Síntese de Membranas de Acetato de Celulose Híbridas e Aplicação do Método Isoconversional de Flynn-Wall-Ozawa

Gesiane Mendonça Ferreira^{1,†}, Daniella Herdi Cariello¹, Filipi Santos França¹, Kelly Cristine da Silveira¹, M. Clara Gonçalves², Mônica Calixto Andrade¹

¹*Polytechnic Institute, Rio de Janeiro State University, Nova Friburgo, Brazil*

²*Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Lisboa, Portugal*

[†]**Gesiane Mendonça Ferreira:** gmferreira@iprj.uerj.br

Abstract

The synthesis of hybrid materials is a promising alternative in the production of materials with optimized properties. In this context, the classic cellulose acetate membranes are being modified. It is worth mentioning that knowing the thermal stability of cellulosic materials is an essential factor in their use since organic polymers have low thermal resistance, limiting their applicability. This work evaluates the synthesis and the study of the thermal degradation kinetics of hybrid cellulose acetate membranes. The synthesis was carried out using the sol-gel process, with the phase inversion technique, through the reaction of cellulose acetate with organometallic precursors: tetraethyl orthosilicate, TEOS; 3-aminopropyl triethoxysilane, APTES, and titanium isopropoxide, TiPOT, in fixed composition. Thermal characterization was performed with thermogravimetric analysis at different heating rates under a nitrogen atmosphere. The kinetic parameter of thermal decomposition activation energy, E_a , was estimated with the isoconversional method proposed by Flynn-Wall-Ozawa (FWO). The degradation kinetics shows that the change in the chemical composition of the samples directly interferes with their thermal properties. Thus, it is possible to observe that the activation energy found for the reference sample, AC-Pure, in the first and second batches was 233.5 and 219.05 kJ/mol, respectively. The composition modification results in an increase in activation energy, in which sample B0//100-30 recorded 310.31 and 226.05 kJ/mol in the first and second batches; and sample B100//0-30 reached 452.73 and 424.74 kJ/mol. It is clear that the increase in the thermal resistance of the samples is associated with the change in the chemical composition and must be attributed to the increase in the TEOS content in the composition due to the formation and increase in the presence of siloxane groups in the material.

Keywords

Hybrids Membranes • Sol-gel Synthesis • Degradation Kinetics • Isoconversional Method • Flynn-Wall-Ozawa (FWO) Method

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Resumo

A síntese de materiais híbridos é uma alternativa promissora na produção de materiais com propriedades otimizadas. Neste contexto, as clássicas membranas de acetato de celulose estão sendo modificadas. Conhecer a estabilidade térmica dos materiais celulósicos é um importante fator na sua utilização, uma vez que os polímeros orgânicos possuem baixa resistência térmica, limitando sua aplicabilidade. Neste trabalho é avaliada a síntese e o estudo da cinética de degradação térmica das membranas de acetato de celulose híbridas. A síntese foi realizada utilizando o processo sol-gel, com a técnica da inversão de fases, através da reação do acetato de celulose com os precursores organometálicos: ortossilicato de tetraetil, TEOS; 3-aminopropil trietoxissilano, APTES, e o isopropóxido de titânio, TiPOT, em composição fixa. A caracterização térmica foi realizada com análise termogravimétrica em diferentes taxas de aquecimento, sob atmosfera de nitrogênio. O parâmetro cinético de decomposição térmica energia de ativação, E_a , foi estimado com o método isoconversional proposto por Flynn-Wall-Ozawa (FWO). A cinética de degradação mostra que a modificação na composição química das amostras interfere diretamente em suas propriedades térmicas. Desta forma, é possível observar que a energia de ativação encontrada para a amostra de referência, AC-Pura, na primeira e segunda batelada, foi de 233,5 e 219,05 kJ/mol, respectivamente. A modificação da composição resulta no aumento da energia de ativação, em que a amostra B0//100-30 registrou 310,31 e 226,05 kJ/mol na primeira e segunda batelada; e a amostra B100//0-30 atingiu 452,73 e 424,74 kJ/mol. O aumento da resistência térmica das amostras está associado à modificação na composição química e pode ser atribuído ao aumento do teor de TEOS, devido à formação e aumento da presença de grupos siloxanos no material.

Palavras-chave

Membranas Híbridas • Síntese sol-gel • Cinética da Degradação • Método Isoconversional • Método de Flynn-Wall-Ozawa (FWO)

1 Introduction

Commercially available inorganic membranes are mainly composed of oxides, such as silica, titania, zirconia, and alumina, which have greater thermal stability. On the other hand, the membranes of organic polymers, such as cellulose acetate (CA), polyamides, and polysulfones, have some limitations. In this context, organic membranes obtained through the synthesis of cellulose acetate present advantages regarding their use, such as biodegradability; abundant raw material sources; the possibility of chemical manipulation, and low cost [1]. However, their sensitivity to chlorine, hydrophobic character and low thermal stability [2] make them unviable and decrease their field of application.

Hybrid cellulose acetate membranes come from chemical modification through the use of organometallic compounds in the molecule to be transformed, resulting in a material with improved properties [3]. Several industrial sectors have explored such materials, especially in the sector of membrane separation. The membranes have the function of separating, fractionating, or filtering solutions, thus presenting pores of various dimensions, which different selection mechanisms and driving forces to promote the separations [4].

In this work, the objective is to synthesize hybrid membranes using the sol-gel process and the phase inversion technique with the incorporation of tetraethyl orthosilicate (TEOS), 3-aminopropyl triethoxysilane (APTES), and titanium isopropoxide (TiPOT) to the cellulose acetate structure. After the synthesis, evaluating the thermodegradative behavior of the obtained membranes is fundamental for the processing techniques and subsequent application. Thus, the study will be guided by the evaluation of the thermal degradation kinetics of the hybrid cellulose acetate membranes under non-isothermal conditions. The kinetic parameter of activation energy, E_a , will be calculated by applying the mathematical method proposed by Flynn-Wall-Ozawa (FWO) with the data obtained by thermogravimetric analysis, TGA, because it is a classic method of studying kinetics found in the literature and due to its easy mathematical application.

2 Materials and Methods

2.1 Materials

The hybrid membranes were synthesized from the following reagents: cellulose acetate (CA), $C_6H_7O_2(OH)_3$, ~30.000 g/mol, $\geq 97\%$, Sigma-Aldrich; tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)_4$, 98%, Sigma-Aldrich; 3-aminopropyl-triethoxysilane (APTES), $C_9H_{23}NO_3Si$, $\geq 98\%$, Sigma-Aldrich; titanium isopropoxide (TiPOT), $C_{12}H_{28}O_4Ti$, Sigma-Aldrich, 97% purity grade; formamide, CH_3NO , $\geq 99.5\%$, Scientific Exodus; acetone, C_3H_6O , 99.7%, Synth; and nitric acid (HNO_3), $\geq 90.0\%$, Synth.

2.1.1 Sol-Gel Synthesis and Phase Inversion Technique

In this work, the hydrolysis and condensation reactions, characteristic of the sol-gel process, were catalyzed in the acid medium in the presence of the precursors TEOS, TiPOT, and APTES being based on previous studies [3,12, 21]. Thus, the synthesis was promoted in situ by adding distilled water, nitric acid, formamide, and acetone to the cellulose acetate (CA) polymer.

The beginning of the application of the phase inversion technique is mixed with the beginning of the sol-gel process, consisting of the formation of a film obtained from a polymeric solution that was subjected to stirring for 24h. Subsequently, the solution presents a gelatinous and homogeneous aspect, followed by the spreading step over a petri dish, where the solvent evaporates for approximately 30 seconds. Finally, the solution is taken to an ice water bath to form the film, separating two liquid phases, the polymer-rich phase and the poor phase, which will originate the pores. The purpose of applying this technique is to form membranes with anisotropic morphology. Thus, membranes of two types were synthesized: pure cellulose acetate membrane and cellulose acetate hybrid membranes, composed of groups that insert silicon, nitrogen, and titanium into the polymeric structure, named series B, according to Table 1 [5].

Table 1: Composition of hybrid cellulose acetate membranes.

Composition (g)	CA-PURE	B0//100-30	B100//0-30
Cellulose acetate	17.00	16.40	16.40
Formamide	30.00	29.00	29.00
Acetone	53.00	51.10	51.10
TEOS	0.00	0.00	2.10
TiPOT	0.00	0.96	0.96
APTES	0.00	2.10	0.00
HNO_3 (drops)	0.00	9.00	9.00
Distilled water	0.00	0.50	0.50
Formulation for 100 g solution	100.00	100.06	100.06

The sample nomenclature is based on the concentrations of the reagents involved in their composition. Thus, it can be understood as "B", referring to the new series of synthesized membranes, since this work follows a line of research on the synthesis of hybrid membranes initiated at the Instituto Superior Técnico, Lisboa, IST [3]. All synthesized samples have a fixed percentage of 95% (m/m) cellulose acetate, with 5% (m/m) for modification with the precursors.

The first number refers to the concentration of TEOS, % (m/m), followed by the amount of APTES, % (m/m), and finally, "30" refers to the pre-fixed amount of TiPOT. It is worth noting that the decision to fix the amount of 1.5% (m/m) in the final composition of the material is based on the study by Peixoto and co-workers [12](2020), which relates the presence of TiPOT to the increase in the parameter of permeability of modified membranes. Thus, 3.5% (m/m) of the final composition was allocated to the evaluation of the presence of segments containing only silicon (TEOS) or silicon and nitrogen (APTES).

2.2 Method

2.2.1 Fourier Transform Infrared Spectroscopy

The hybrid membranes were analyzed using infrared spectroscopy with an attenuated total reflectance (ATR) accessory, Pike Miracle Single Reflection ATR from Pike Technologies, on a PerkinElmer Frontier FTIR spectrometer and sampling accessory. The analysis was performed under standard conditions, with a 4 cm^{-1} resolution and 256 scans. All spectra were plotted using *Scidavis* software.

2.2.2 Thermal Analysis

The analyses were performed under non-isothermal conditions, with a temperature range from 30 to 600 °C, at heating rates (β) of 5, 10, and 20 °C/min, under a continuous flow of 20 mL/min of nitrogen and mass of the samples fixed at approximately 6 mg. This technique was performed on the STA 6000 Simultaneous Thermal Analyzer, Perkin Elmer.

2.2.2.1 Degradation Kinetics

The thermal degradation kinetics occurs using experimental data obtained through thermal analysis [6]. Thus, as the change in mass is measured, one can define the degree of conversion as a function of measured mass loss, as shown by Eq. (1):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (1)$$

The definition of the variables is given by: m_0 is the initial mass of the sample; m_t is the mass in time t and m_f is the mass at the end of the process.

Through the use of mathematical relationships, the fundamental equation of the kinetic study can be related to the Arrhenius equation, enabling the rewriting of the reaction variation based on a single-step process, defined by Eq. (2) [7]:

$$\frac{d\alpha}{dt} = kf(\alpha) = A \exp\left(-\frac{Ea}{RT}\right) f(\alpha) \quad (2)$$

where T (K) is the temperature, k is the reaction rate constant and is described by Arrhenius' law, and R ($8.314\text{ JK}^{-1}\text{mol}^{-1}$) is the ideal gas constant. The remaining variables from the Arrhenius equation, Ea , A and $f(\alpha)$ are kinetic parameters and the activation energy, the pre-exponential factor, and the reaction model, respectively.

Since the data are obtained by analysis under non-isothermal conditions, it is necessary to include the term representing the heating rate, as noted in Eq. (3):

$$\beta \left(\frac{d\alpha}{dT}\right) = A \exp\left(-\frac{Ea}{RT}\right) f(\alpha) \quad (3)$$

2.2.2.2 Fynn-Wall-Ozawa Isoconversional (FWO) Method

By definition, isoconversional methods are known as "free model" methods. They can obtain the activation energy parameter for each conversion degree without being required to know the model governing the reaction [8]. For example, the Fynn-Wall-Ozawa (FWO) method describes a plot of $\log \beta$ versus $1/T_p$ that generates a straight line whose slope can be used to estimate the activation energy without any assumptions about the integral function, $g(\alpha)$ [9]. However, for FWO, Eq. (4), the use of the Doyle approximation is required, and its mathematical model is described below:

$$\log \beta = \log\left(\frac{AEa}{Rg(\alpha)}\right) - 2.315 - 0.4567\left(\frac{Ea}{RT}\right) \quad (4)$$

3 Results and discussion

3.1 Fourier Transform Infrared Spectroscopy

By analyzing the spectral data presented in Fig. 1, the acetylated materials have a highlighted intensity increase in the band around 1749 cm^{-1} , attributed to the stretching of the C=O of the carbonyl groups [10]. Moreover, the band at 1243 cm^{-1} is attributed to the stretching of the C-O-C bond from the acetate, while the band at 1048 cm^{-1} is a characteristic band of the acetylated materials. Notably, a weak band centered at 903 cm^{-1} confirms the presence of acetate methyl groups in all the examined compositions.

Another band that stands out is given around $3000\text{--}3700\text{ cm}^{-1}$ and is attributed to the O-H stretch of the hydroxyl groups, coming from contributions from water molecules (H-O-H) for the pure cellulose acetate membrane and the hydrolyzed silica and titania precursors ($\equiv\text{Si-OH-}$, $\equiv\text{Ti-OH-}$) for the hybrid membranes, agreeing with studies previously carried out [11, 3, 12]. For the regions between $1690\text{--}800\text{ cm}^{-1}$ and $950\text{--}1175\text{ cm}^{-1}$, the Ti-O-C peaks are expected and are better visualized with more detailed analysis, such as a deconvolution study [12]. In the B100//0-30 membrane, which has the silicon-based precursor, the increasing peak at 980 cm^{-1} is attributed to the Si-O stretching vibration, belonging to the Si-OH group [10]. In contrast, the absorption band at approximately 1050 cm^{-1} is attributed to the Si-O-Si stretching vibration [13]. The spectra are very similar, so it is necessary to highlight the differences between the AC-Pure membrane and the hybrid membranes in the carbonyl stretching region, $1680\text{--}1800\text{ cm}^{-1}$ [12]. From the presence of bonds and functional groups characteristic of the materials of the samples, it is possible to state that the synthesis of the membranes occurred efficiently, allowing from these results, to proceed with studies of the thermal behavior of chemically modified membranes.

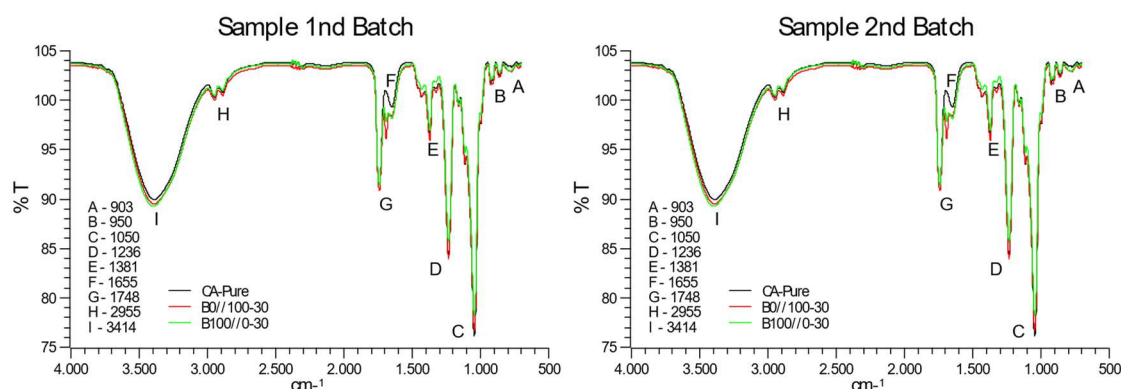


Figure 1: Main absorption bands in the infrared spectrum.

3.2 Thermal Analysis

Figure 2 presents the thermogravimetric (TG) and its derivative (DTG) curves for the cellulose acetate hybrid membranes. As can be observed, both the TG and DTG curves evidence the presence of three stages of decomposition, coming in agreement with data reported in the literature for membranes based on cellulosic materials [3, 5, 14, 15, 16]. The first stage of decomposition of CA-PURE membranes, B0//100-30 and B100//0-30 occurs at a temperature below $100\text{ }^{\circ}\text{C}$, which may be related to the evaporation of absorbed wastewater or solvents remaining from the synthesis process [16], with an average mass loss of 12, 13, and 19%, respectively, in the two synthesized batches.

The second decomposition stage, which occurs in the range of $135\text{ }^{\circ}\text{C}$ to $270\text{ }^{\circ}\text{C}$, for the two batches evaluated, is attributed to the phase of the beginning of the decomposition of cellulose acetate chains. Also, this stage is related to the loss of functional groups, melting of cellulose acetate crystals [17], breaking of bonds in the CA structure, decomposition of ammonium and oxygen-containing functional groups, and the possible onset of thermal degradation of TiPOT [13, 18]. This degradation of the segment with titanium accounts for about 56, 61, and 47% of the mass loss degradation process of the CA-PURE, B0//100-30, and B100//0-30 samples, respectively.

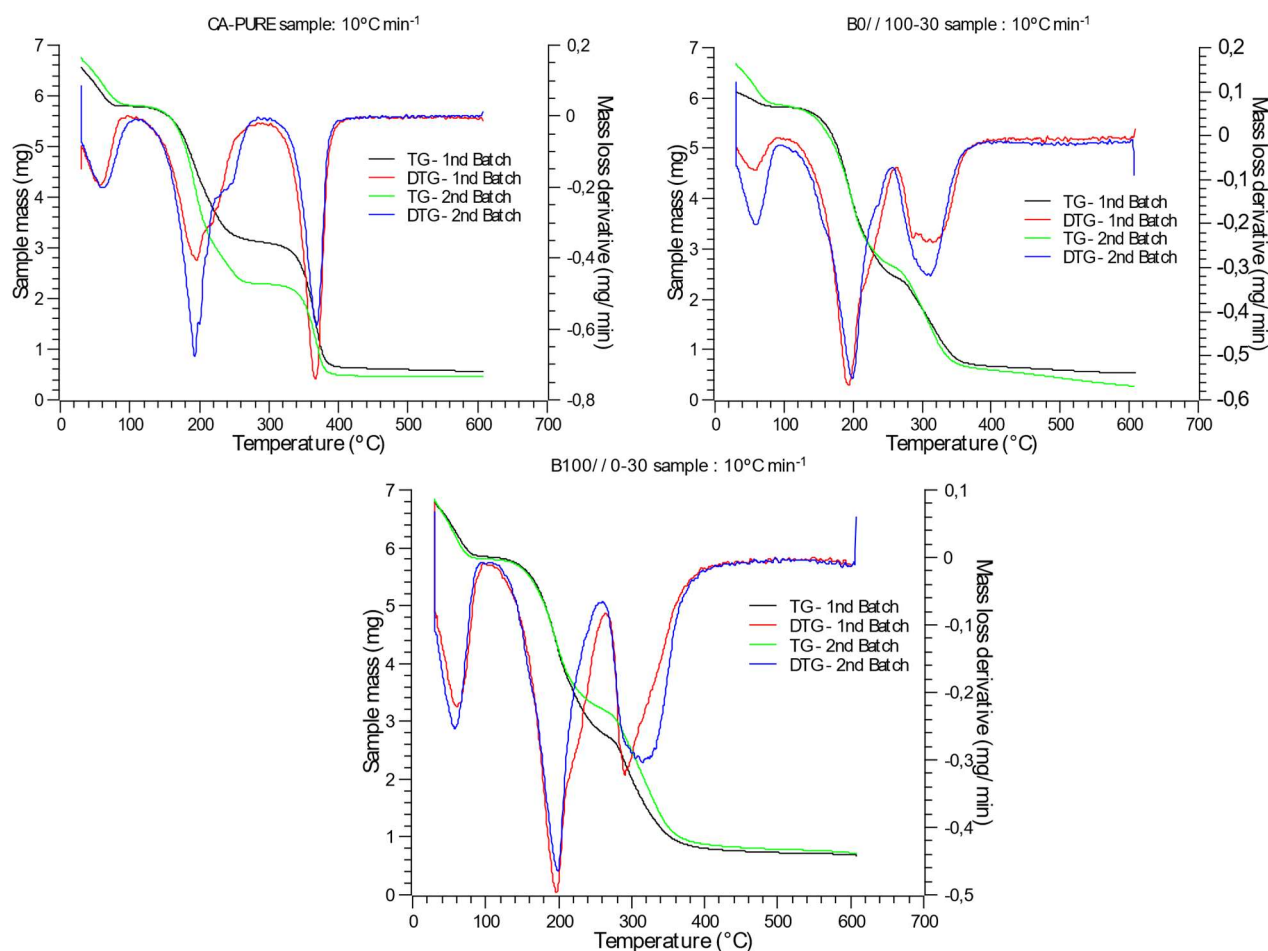


Figure 2: TG and DTG curves of pure cellulose acetate and hybrid membranes.

The third stage of decomposition occurs in the range of 300 °C to 405 °C. This stage is associated with the degradation of cellulose acetate [17], followed by the formation of carbonized material and thermal degradation associated with TiPOT around 400 °C. Also, it is associated with the mass loss corresponding to the degradation of the aminopropyl groups of APTES, which occurs specifically from 320 °C [19, 17], i.e., at this stage, the material is already degraded [11, 16]. This stage presents a mass loss equivalent to 32% for the CA-PURE sample, 26% for the B0//100-30 sample, and 34% for the B0//100-30 sample. The interval from 180 to 380 °C is attributed to the highest mass loss due to the intense degradation of cellulose acetate since this component is found in larger quantities in the samples [17].

Analyzing the behavior of the TG and DTG curves, Fig. 2, it was clear that the thermal behavior of the thermograms is similar, with only minor variations in the start and end temperatures of the degradation stages. Thus, thermogravimetric analysis alone does not explain how changing the chemical composition alters the thermal properties. Given this, it is necessary to study the kinetics of degradation through the correlation of experimental thermal data with mathematical methods to verify how changes in composition interfere with the structural and chemical changes of cellulose acetate membranes.

3.2.1 Degradation Kinetics

Figure 3 presents the result of the linearization of Eq. 4, which was generated using conversion degrees from 10 to 80% mass loss, taking in intervals of 10%, resulting in distinct E_a values for each conversion degree. It is possible to observe small changes in the angular coefficient of the hybrid cellulose acetate membrane samples compared to the AC-Pure sample. Interestingly, the isoconversion lines exhibited an irregular behavior, up to a conversion degree of 40%. After 50%, they became increasingly regular as the degradative process progressed. This change in behavior suggests that the scission of bonds with similar energy levels was broken as the degradation process advanced. According to reference studies [14,15,20], these variations of the curves and, consequently, activation energy at the beginning of the degradative process suggest that the initial stages of the degradative process entail a series of

parallel, successive, and competitive reactions with varying energy levels, as well as scissions and interactions between the components of the samples. This complexity further underscores the intricate nature of the degradation process.

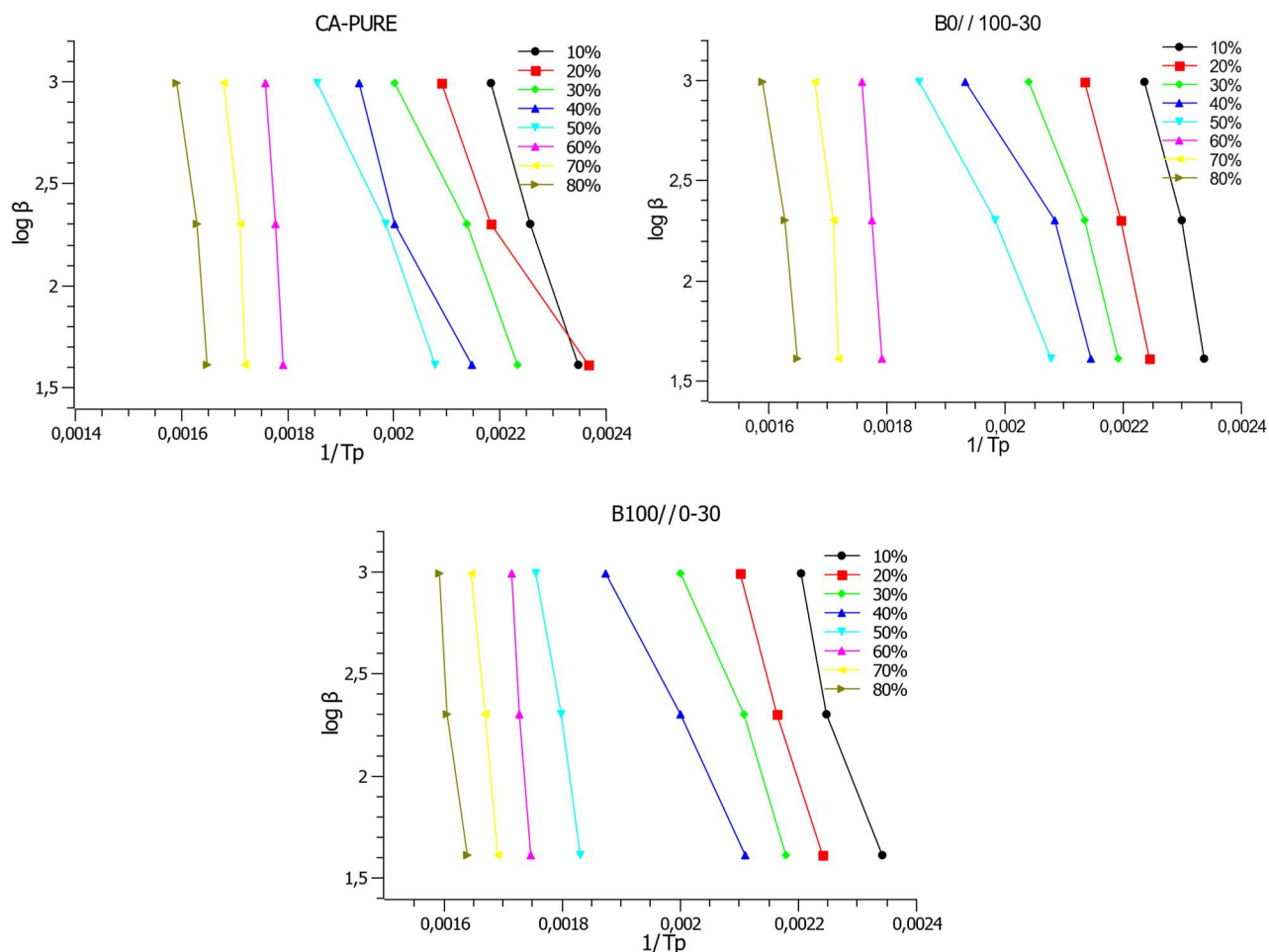


Figure 3: Isoconversional plot of $\log(\beta)$ as a function of the inverse of temperature ($1/T_p$).

In Fig. 4, the relationship of activation energy as a function of the degree of mass conversion is presented, which indicates the existence of a dependence of activation energy (E_a) with the degree of conversion (α), i.e., it shows that the kinetic reaction mechanism involved in the degradative process is not straightforward in hybrid samples. Thus, subjecting this type of material to continuous heating entails bond breaking in the primary and side chains, and substituent groups and vaporization of resulting fragments may occur, leading to a series of new reactions. This complexity is reduced for pure cellulose acetate membranes, where the curve presented in Fig. 4 has a more uniform profile.

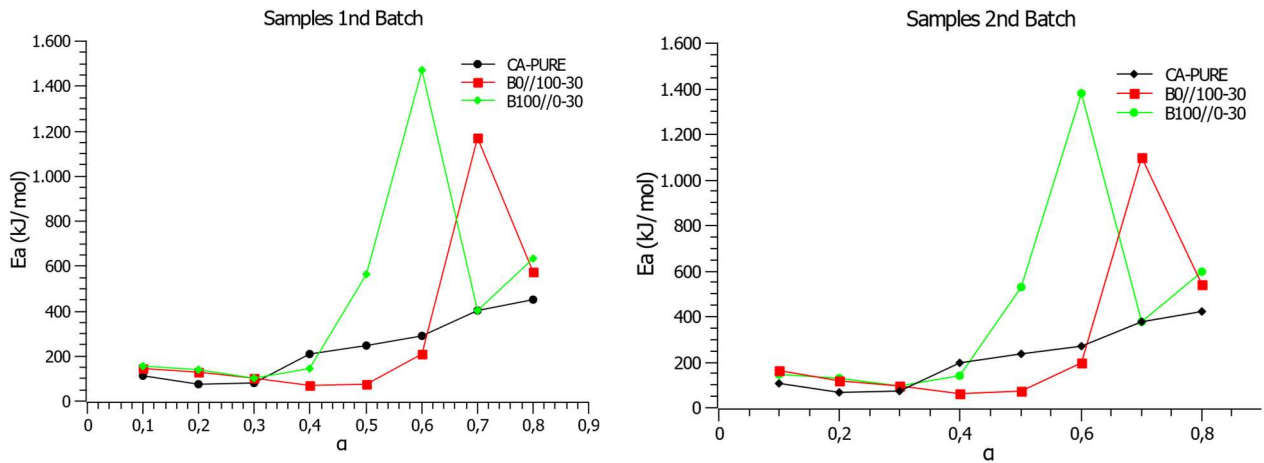


Figure 4: Activation energy as a function of the degree of mass conversion.

Upon analysis of the data presented in Fig. 4 and Table 2, it is observed that the FWO method indicates that the the activation energy levels of hybrid membranes, B0//100-30 and B100//0-30, are higher compared to the reference membrane, CA-PURE. Furthermore, the method allows the calculation of the activation energy by the slope of the curve for a given value of α . Nonetheless, it is worth noting that the mathematical approximation employed to determine the slope requires correction, as outlined in Eq. (5).

$$Slope = -Ea \left(\frac{0.4567}{R} \right) \tag{5}$$

Table 2: Activation energy of degradation of hybrid cellulose acetate membranes, of the first and second batches, by the FWO method.

α (%)	CA-PURE (First)		CA-PURE (Second)		B0//100-30 (First)		B0//100-30 (Second)		B100//0-30 (First)		B100//0-30 (Second)	
	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²
10	113.20	0.92	106.20	0.98	147.61	0.98	163.82	0.91	157.41	0.92	147.68	0.93
20	73.33	0.96	68.79	0.90	128.84	0.97	117.14	0.95	138.74	0.96	130.16	0.98
30	80.87	0.90	75.81	0.92	101.59	0.98	95.31	0.91	103.97	0.89	97.54	0.83
40	210.96	0.95	197.92	0.89	68.05	0.97	63.84	0.93	147.40	0.76	138.29	0.81
50	249.65	0.97	234.22	0.97	77.07	0.96	72.31	0.93	563.22	0.87	528.41	0.89
60	289.00	0.99	271.14	0.99	210.33	0.79	197.33	0.80	1470.00	0.92	1379.15	0.91
70	401.71	0.78	376.88	0.89	1172.67	0.94	1100.18	0.96	404.82	0.97	379.80	0.90
80	449.28	0.82	421.51	0.81	576.37	0.97	540.75	0.95	636.24	0.93	596.92	0.91
Mean	233.50		219.05		310.31		226.24		452.73		424.74	

The application of the FWO method was satisfactory for all samples analyzed since most of the correlation coefficients found were close to 1.0. In contrast, the lower coefficients can be explained due to flaws obtained during the synthesis that caused noise that affected the thermogravimetric analysis and the data used for the activation energy calculations. Another point to be highlighted is that the addition of TEOS, APTES, and TiPOT increased the activation energy of all membranes compared to the CA-Pure sample, thus hindering its thermal degradation. This chemical modification is consequently attributed to higher thermal and chemical stability. Also, it is observed that the sample modified with the organometallic TEOS, B100//0-30, has greater thermal stability compared to the

composition with the insertion of silicon and nitrogen, B0//100-30. This fact can be explained due to the greater presence of siloxane groups (Si-O-Si) in the structure of the membrane, which is responsible for improving the thermal properties.

4 Conclusion

In this work, the synthesis and evaluation of thermal degradation kinetics were performed for pure cellulose acetate membranes and hybrid membranes modified with silicon, nitrogen, and titanium-based compounds. The size, physical surface appearance, and color of all membranes were similar. The spectra obtained by FTIR-ATR spectroscopy reveal the presence of the organometallic compounds and the CA, the base material of the membranes, attesting to the synthesis process. The results obtained from the thermal analysis, TG/DTG, showed that the synthesized samples have a thermal behavior equivalent to the cellulose acetate samples evaluated in the literature. The degradation process is complex and may involve multiple reactions. However, only the interpretation of the data extracted from the thermogravimetric analysis cannot explain how the different compositions interfere with thermal stability. The investigation into degradation kinetics, utilizing the isoconversional FWO method, has demonstrated that the B100//0-30 sample, which contains the highest concentration of silicon-based groupings, possesses the highest activation energy when compared to both the pure cellulose acetate membrane, AC-pure, and the hybrid cellulose acetate membrane, B0//100-30. As a result, the B100//0-30 sample exhibits superior thermal stability. Hence, it is apparent that the thermal stability of hybrid membranes is intricately linked to the increased concentration of silanol and siloxane groups.

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