VETOR

Evaluation of Thermal Degradation Kinetics of Hybrid Cellulose Acetate Membranes using Isoconversional Methods[☆]

Avaliação da Cinética de Degradação Térmica de Membranas de Acetato de Celulose Híbridas usando Métodos Isoconversionais

Gesiane Mendonça Ferreira[1,†], Daniella da Silva Herdi[1], Kelly Cristine da Silveira[1], M. Clara Gonçalves[2], Mônica Calixto de Andrade[1]

[1]*Polytechnic Institute, State University of Rio de Janeiro, Nova Friburgo, Brazil*
[2]*Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Lisboa, Portugal*

[†]**Gesiane Mendonça Ferreira:** gesiane_mf@hotmail.com

Abstract

Cellulose acetate membranes are widely used in industry, emphasizing water purification processes, such as desalination. With some limiting mechanical properties, the synthesis of hybrid membranes appears as an alternative for developing high-performance materials. For its application, knowledge of thermal stability is crucial. In this work, the thermal degradation kinetics of AC-SiO_2-$(CH_2)_3NH_2$ hybrid cellulose acetate membranes are evaluated from thermogravimetric analysis, at three heating rates, 5, 10, and 20 °C/min. The isoconversional methods proposed by Kissinger, Flynn-Wall-Ozawa, and Friedman were used for the present study of degradation kinetics. It was observed that insertion of silicon to polymeric structure promoted thermal stability to the membrane, presenting higher activation energy than pure cellulose acetate membrane, increasing from 240.28 to 1039.01 kJ/mol, using the method of Friedman. In contrast, the increase in nitrogen concentration decreases its thermal stability compared to the cellulose acetate membrane with incorporated silicon, reducing the activation energy from 1039.01 to 250.50 kJ/mol. However, it is more stable than the pure cellulose acetate membrane. The evaluation carried out in this study explained the influence of the minimum variation in the chemical composition against the thermal stability of hybrid membranes, being a factor of great importance for its application.

Keywords

Degradation Kinetics • Cellulose Acetate Membranes • Hybrid Membranes • Isoconversional Methods

Resumo

As membranas de acetato de celulose são amplamente utilizadas na indústria, nos processos de purificação de água, principalmente na dessalinização. Com algumas propriedades limitantes, a síntese de membranas híbridas aparece como uma alternativa para o desenvolvimento de materiais de alto desempenho. Para sua aplicação, o conhecimento da estabilidade térmica é crucial. Neste trabalho, a cinética de degradação térmica de membranas

---

[☆] This article is an extended version of the work presented at the Joint XXIV ENMC National Meeting on Computational Modelling and XII ECTM Meeting on Science and Technology of Materials, held in webinar mode, from October 13th to 15th, 2021.

híbridas de acetato de celulose AC-SiO_2-$(CH_2)_3NH_2$ é avaliada a partir de análise termogravimétrica, em três taxas de aquecimento, 5; 10 e 20 °C/min. Os métodos isoconversionais propostos por Kissinger, Flynn-Wall-Ozawa e Friedman foram usados para o presente estudo da cinética de degradação. Observou-se que a inserção do silício na estrutura polimérica promoveu estabilidade térmica à membrana, apresentando energia de ativação superior à membrana de acetato de celulose puro, passando de 240,28 para 1039,01 kJ/mol, pelo método de Friedman. Em contraste, o aumento na concentração de nitrogênio diminui sua estabilidade térmica em relação à membrana de acetato de celulose com silício incorporado, reduzindo a energia de ativação de 1039,01 para 250,50 kJ/mol. No entanto, é mais estável do que a membrana de acetato de celulose pura. A avaliação realizada neste estudo explicou a influência da variação mínima na composição química contra a estabilidade térmica de membranas híbridas, sendo um fator de grande importância para sua aplicação.

Palavras-chave

Cinética de Degradação • Membranas de Acetato de Celulose • Membranas Híbridas • Métodos Isoconversionais

1 Introduction

The combination of components with different physical properties has led to the formation of materials with optimized characteristics and properties different from those that originated them. Hybrid materials are obtained from the combination of homogeneous solutions made up of organic and inorganic components. The inorganic phase is usually dispersed on a nanometric scale and linked to the organic matrix through covalent bonds. Colloidal particles can be synthesized through the molten state, solution, *in situ* polymerization, or sol-gel process. These techniques give the compound excellent mechanical, chemical, and thermal properties and prove the existence of simultaneous action of components of the organic segments, which are responsible for superior mechanical properties related to the processability and stability of inorganics [1].

The wide application of hybrid compounds has been highlighted in the manufacture of membranes, which work as semi-permeable physical barriers for separating two phases present in a solution, restricting the passage of solute from one phase to another. As a base raw material for the preparation of hybrid membranes, the use of cellulose acetate (CA) stands out. It is an ecological polymer derived from the acetylation of cellulose, produced through the esterification of naturally abundant materials, such as wood and cotton. Due to the accessibility of its raw material, AC has a low cost, in addition to the possibility of combining properties such as optical transparency and a highly smooth surface.

However, cellulose acetate has some properties that can be considered an obstacle depending on its application, such as its hydrophilic character, which is responsible for the unsatisfactory mechanical properties of these materials in humid environments and low thermal stability, a strong characteristic of polymeric materials; low mechanical strength; low chemical resistance; sensitivity to cleaning agents and low resistance to scale [2]. As a strategy to improve some of these properties, the insertion of additives is successfully reported in the literature. The incorporation of silicon-based groups in the structure of cellulose acetate (AC/SiO_2) [3] and titanium (AC/TiO_2) [4] presents a significant improvement in the mechanical performance and hydraulic permeability; on the other hand, the insertion of silicon- and nitrogen-based groups, forming hybrid membranes of the AC-SiO_2-$(CH_2)_3NH_2$ type, showed an increase in the degrees of freedom (chemical and structural), improving chemical selectivity and providing improved hydraulic permeability [2]. The properties achieved with nitrogen-based hybrid membranes encourage the development of new high-performance structures.

For the processing and use of polymers, thermal stability is a limiting factor, one of these materials' main disadvantages. Traditionally, polymers are prepared at processing temperatures in the range of 100 to 300 °C and even lower usage temperatures. Above the specified ranges, thermodegradation processes can already be observed, giving a restrictive character to using these materials [5].

Degradation can be understood as a set of chemical and physical reactions, a complex process of different initiators, which can cause significant changes in material properties. Degradation can alter mechanical, thermal, and electrical properties and compromise structural or surface performance, as it limits the visual appearance of the polymeric material, especially its color. Degradation can occur in a wide variety of environments, under different conditions caused by chemical or physical attacks, resulting from a combination of degrading agents and other mechanisms, causing irreversible changes in the properties of polymeric materials.

In this context, understanding the degradation behavior of these materials and their thermal degradation kinetics is crucial for processing and application. Accordingly, the present work evaluates the thermal degradation mechanism of a series of new hybrid cellulose acetate membranes of the AC-SiO_2-$(CH_2)_3NH_2$ type under non-isothermal conditions. The activation energies are determined through the proposed methods by Flynn-Wall-Ozawa (FWO), Friedman, and Kissinger. The evaluation is performed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA/DTG).

2 Materials and Methods

2.1 Materials

The hybrid membranes used in this work were synthesized from the following reagents: cellulose acetate (AC), $C_6H_7O_2(OH)_3$, ~30,000 g/mol, ≥ 97%, produced by Sigma-Aldrich; tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)_4$, 98%, manufactured by Sigma-Aldrich; 3-aminopropyl-triethoxysilane (APTES), $C_9H_{23}NO_3Si$, ≥ 98%, manufactured by Merck; formamide, CH_3NO, ≥ 99.5%, produced by Carlo Erba Reagents; acetone, C_3H_6O, 99.7%, manufactured by Labchem; and nitric acid (HNO_3), ≥ 90.0%, made by ACS. No reagent used in the synthesis or drying has undergone prior purification. All samples were synthesized at the Department of Chemical Engineering, Instituto Superior Técnico, University of Lisbon, Portugal, and used as raw material for this study of degradation kinetics.

2.1.1 Synthesis of Hybrid Membranes

The synthesis of hybrid membranes is based on combining the sol-gel and the phase inversion techniques. The sol-gel process consists of forming particles in colloidal size (sol) and consequent three-dimensional network (gel) from precursors in its synthesis route, which causes chemical reactions of hydrolysis and condensation. The alkoxide is the most used compound in the sol-gel approach due to its ease of promoting hydrolysis reactions, such as tetraethyl orthosilicate (TEOS) [6]. The phase inversion method enables the production of asymmetric membranes and prepares the polymer solution from the following reagents: cellulose acetate, tetraethyl orthosilicate, 3-aminopropyl-triethoxysilane, acetone, formamide, nitric acid, and water [2].

The synthesis occurs in an acidic medium, causing structural changes in the polymer, like more extensive branching with a more open and less dense three-dimensional network, which occurs because the hydrolysis reaction happens faster than the condensation reaction in the sol-gel transition. The mixture, prepared with all the reagents, is stirred until complete homogenization for 24 hours. Then, it is deposited on a glass plate with the help of a spreading knife until the solution is uniformly disposed of so the solvent evaporation phase can take place. Next, the glass plate is placed in a coagulation bath (water at 0 °C) for 30 min. Finally, the membranes are removed from the glass plate and washed with deionized water to remove traces of solvent, followed by storage in water at 4 ± 1 °C [2].

The samples used in this study have a fixed percentage of 95 wt% of cellulose acetate, with 5 wt% for modification with TEOS or APTES, and are therefore called A5. The functionalization was carried out in the cellulose acetate structure at different concentrations with silicon and nitrogen species. The sample nomenclature refers to the insertion of the nitrogen group from the APTES precursor, varying in the following percentages: 0; 5; 10; 20; 30, and 50 wt%. The samples are named according to their composition, as shown in Table 1.

Table 1: Composition of hybrid cellulose acetate membranes

Composition (g)[a]	AC-pure	A5-00	A5-05	A5-10	A5-20	A5-30	A5-50
Cellulose acetate	17.00	16.40	16.40	16.40	16.40	16.40	16.40
Formamide	30.00	29.00	29.00	29.00	29.00	29.00	29.00
Acetone	53.00	51.10	51.10	51.10	51.10	51.10	51.10
TEOS	0.00	3.00	2.85	2.70	2.40	2.10	1.50
APTES	0.00	0.00	0.16	0.32	0.64	0.96	1.50
Bi-distilled water	0.00	0.50	0.50	0.50	0.50	0.50	0.50
HNO_3 (drops)	0	6	9	9	9	9	9
Silicon functionalization percentage (TEOS)[b]	0 %	100%	95%	90%	80%	70%	50%
Nitrogen functionalization percentage (APTES)[b]	0%	0%	5%	10%	20%	30%	50%

[a] *The composition is based on the formulation of 100 g of solution.*

[b] *Cellulose acetate composition remains the same in all functionalized samples, 95 wt%.*

2.1.2 Thermal Analysis

Thermogravimetric analyses (TGA) were performed at Biomaterials Laboratory, IPRJ/UERJ, with the Simultaneous Thermal Analyzer STA 6000, PerkinElmer, in a nitrogen atmosphere with a continuous flow of 20 mL/min, at heating rates *(β)* of 5, 10, and 20 °C min^{-1}, with a temperature range of 30 to 600 °C.

2.1 Methods

The determination of kinetic parameters involves the application of mathematical methods [7]. The knowledge of the degree of conversion (α) is essential to identify the triplet of kinetic parameters (activation energy (E_a), the frequency factor (A) and the reaction model $f(\alpha)$), responsible for determining the degradation mechanism and behavior thermal of the material. The evaluation of such parameters can be applied according to Eq. (1):

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \tag{1}$$

where, $\frac{d\alpha}{dt}$ is the conversion rate of degradation at a constant temperature, $k(T)$ is the degradation rate constant, and $f(\alpha)$ is the reaction model. The degree of conversion can be obtained from the mass ratios at a given temperature or time, expressed by Eq. (2):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}, \tag{2}$$

where, m_0 is the initial mass, is the mass obtained in estimated time or temperature, and m_f is the final mass at the analyzed instant. To stipulate the value of the reaction velocity constant, k, it is necessary to apply the concept of the Arrhenius Equation, which calculates the variation of the rate constant of a chemical reaction with temperature. Through Eq. (3), it is possible to demonstrate the relationship between kinetic parameters, activation energy, and pre-exponential or frequency factors.

$$k = A\exp\left(-\frac{E_a}{RT}\right), \tag{3}$$

where, A (min^{-1}) is the pre-exponential factor, E_a (kJ mol^{-1}) is the activation energy, (8.314 JK^{-1} mol^{-1}) is the universal gas constant, and T is the absolute temperature. By combining Eqs. (1) and (3), the conversion rate equation, Eq. (1), can be rewritten according to Eq. (4). The application of the Arrhenius equation is related to a combination of interpretation of data obtained experimentally with physical understanding.

$$\frac{\mathrm{d}\alpha}{\mathrm{dt}} = \mathrm{Aexp}^{\left(-\frac{E_a}{\mathrm{RT}}\right)}. \tag{4}$$

Under non-isothermal experimental conditions, time dependence is eliminated according to Eq. (5).

$$\beta\left(\frac{\mathrm{da}}{\mathrm{dT}}\right) = \mathrm{A}\,\mathrm{exp}^{\left(-\frac{E_a}{\mathrm{RT}}\right)}\,\mathrm{f}(\alpha). \tag{5}$$

$\beta\left(\frac{\mathrm{dT}}{\mathrm{dt}}\right)$ *i*s the rate of heating, at which the temperature of sample gradually increases in intensity.

2.2.1 Isoconversional Methods

Isoconversional methods are widely used to study the non-isothermal degradation of solid materials; through them, it is possible to estimate the activation energy values (E_a) independently of other parameters that constitute the kinetic triplet. Kinetics is based on isoconversional methods, differentials, such as Friedman, and integrals, such as Flynn-Wall-Ozawa. The Kissinger method is also noteworthy due to its relative simplicity in obtaining the necessary data to calculate the activation energy [7]. Briefly, these methods [7] are described below.

Kissinger's isoconversional method

This method can be applied regardless of the conversion degree, assuming that the degree of conversion has a maximum value at the peak temperature (Tp). A graph of ln (β/Tp^2) versus 1/T provides E_a from the slope of the linear curve, being possible to determine through Eq. (6):

$$ln\left(\frac{\beta}{Tp^2}\right) = \left(-\frac{Ea}{RTp}\right) + ln\left(\frac{AR}{E_a}\right). \tag{6}$$

Friedman's isoconversional method

Friedman's model is considered the most efficient as it uses a real heating rate in its analysis, achieving more accurate results when compared to other methods. The values of E_a can be used through adjustments in $ln\left(\frac{d\alpha}{dt}\right)$ *versus* $\left(\frac{1}{T}\right)$ whose slope of the line will determine the value of the activation energy. The calculation for this new rate is performed from the linear relationship of the curve generated between the data of analysis time (s) *versus* actual sample temperature (°C). From the slope of the line, the real heating rate (real β) is found. Such a method must be applied according to Eq. (7):

$$ln\left(\frac{d\alpha}{dt}\right) = ln\big(Af(\alpha)\big) - \frac{E_a}{RT}, \tag{7}$$

Flynn-Wall-Ozawa integral isoconversional method (FWO)

This method considers a predetermined heating rate, often generating distortions in the value of Ea. It assumes that the degree of conversion function remains constant for all conversion values α, at different heating ratios β. Using mathematical approximations, the simplified model for the FWO method is described in Eq. (8):

$$log\,\beta = log\left(\frac{AE_a}{Rg(\alpha)}\right) - 2.315 - 0.4567\left(\frac{E}{RT}\right) \tag{8}$$

3 Results and discussion

Thermogravimetric analyses were performed at three heating rates, aiming for the thermal degradation study of hybrid cellulose acetate membranes. Figure 1 shows the thermogravimetry (TG) curves for all samples evaluated in this work, at heating rates of 5, 10, and 20 °C/min. Thermogravimetry analysis allows the degradation process to be observed in three stages, with all samples and heating rates evaluated. This behavior is best visualized with the derivative of the thermogravimetric curve (DTG), shown in Fig. 2 for sample A5-00.

The first step, starting at approximately 30 °C, ends below 100 °C. The second degradation step takes place at about 125 °C, finishing at around 224 °C. The temperature range in which the third stage of degradation begins appears at approximately 290 °C and ends above 405 °C. The beginning of the degradation process is attributed to the first stage, with the loss of residual water or volatiles from the synthesis process. There is the loss of functional groups for the second stage, breaking important bonds for the CA structure, as explained by Souza [8]. In this temperature range, the main degradation of cellulose occurs, according to Miranda [9], where the kinetic parameters of thermal decomposition of lignocellulosic residues were demonstrated, in the temperature range from 290 °C to 360 °C, with an intense loss of structure mass. For the third stage, the sample is in an advanced state of degradation. Most of the sample mass loss is attributed to carbonized fragments of the main chain, as Souza [8] explained, who studied the thermal analysis of acetate cellulose propionate.

There is a critical difference in the composition of the membranes synthesized in this work. The classical thermogravimetric analysis could not acknowledge these differences. Therefore, a more detailed study, for instance, the degradation kinetics, is essential to verify the structural and chemical changes carried out in cellulose acetate membranes. The pure cellulose acetate membrane (CA-pure) had the lowest activation energy by the Kissinger method, as shown in Table 2, presenting a more negligible difference concerning the membrane with the highest concentration of nitrogen, A5-50. Therefore, the incorporation of silicon and nitrogen in the cellulose acetate chains may be related to the greater resistance to thermal degradation observed. However, this issue needs to be further investigated, as the Kissinger method has its limitations. Kissinger's approach assumes that activation energy does not vary as a function of the conversion degree. Calculations are made with only the peak temperatures derived from the thermogravimetric analysis for each heating rate. However, the literature shows an influence of the conversion degree on the activation energy. Therefore, in this work, the FWO method was also used, which considers the activation energy.

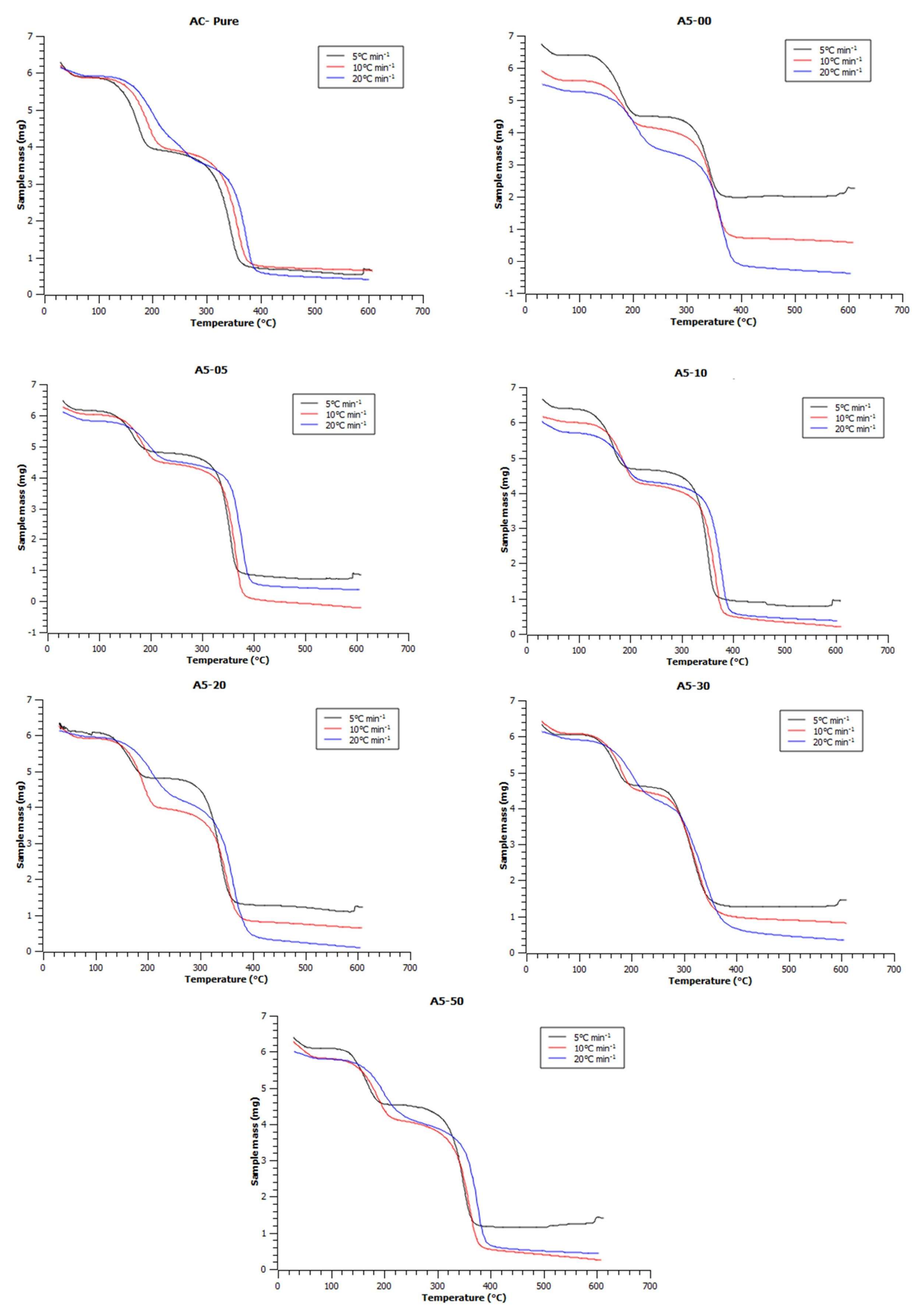

Figure 1: TG curves for pure cellulose acetate membrane and series of hybrid cellulose acetate membranes at different heating rates.

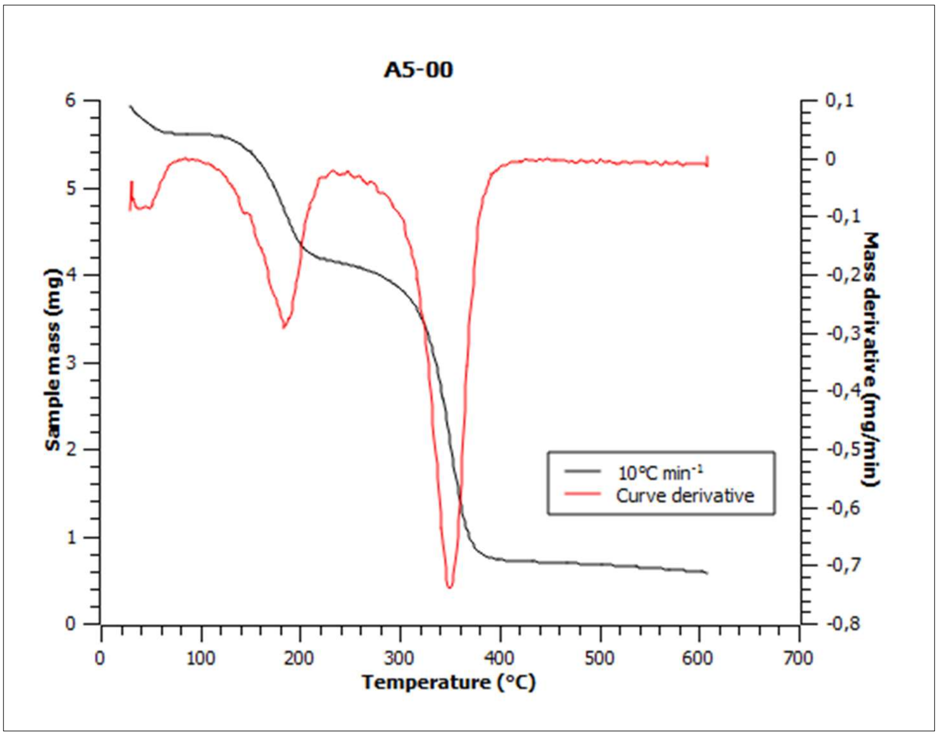

Figure 2: TG and DTG curves for the A5-00 hybrid cellulose acetate membrane.

The application of the FWO method also showed an increase in the activation energy for the hybrid membranes compared to pure cellulose acetate membrane (AC-pure). It has a significant increase in the composition with the addition of only silicon (A5-00). On the other hand, incorporating nitrogen promoted decreased activation energy compared to samples with silicon only. Nevertheless, this decrease did not reach the value of the pure cellulose acetate membrane. As shown in Table 2, there was no consistency between the increase in nitrogen concentration and the variation in activation energy. The FWO Method is simple and easy to apply. It is the most found in degradation kinetic studies and considers the variation of activation energy with the conversion degree of mass loss. However, its formulation uses mathematical approximations, such as Doyle's, which attributes substantial errors to determine the activation energy.

Table 2: Activation energy of degradation of hybrid cellulose acetate membranes, determined by three methods.

Sample	Average	Average E_a – FWO (kJ/mol)	Average E_a-Friedman (kJ/mol)
AC-pure	154.89	137.98	240.28
A5-00	199.01	381.51	1039.01
A5-05	220.40	179.99	319.97
A5-10	169.68	157.10	321.94
A5-20	170.55	188.91	321.20
A5-30	209.17	151.93	290.91
A5-50	160.61	175.83	250.50

The same behavior was observed for the Friedman method; the hybrid samples' activation energies were higher than the pure cellulose acetate membrane. However, all activation energies were higher than Kissinger and FWO methods. In addition to not showing relevant variation in samples A5-05, A5-10, and A5-20, the change in nitrogen concentration in this range, did not influence the activation energy. In contrast, when the increase in nitrogen concentration is significant, the thermal stability decreases for the A5-30 and A5-50 membranes; the activation energy decreases, moving towards values close to those of pure cellulose acetate membranes. Friedman's method is the most recommended method by ICTAC, and it is a derivative method that does not use mathematical approximations. It considers the loss of mass as a function of the conversion degree and uses the real heating rate in its calculations, making it even more different from other methods. Using this real heating rate makes the activation energy results less error-prone and closer to reality, making it the most reliable method. The activation energy of all samples was higher when calculated using the Friedman method. The variation in the chemical composition of the membranes synthesized, and evaluated in this work, can be observed as an influence on the parameters of degradation kinetics; likewise, it has a significant effect on hydraulic permeability and mechanical properties evaluated in the work of Andrade et al. [2].

4 Conclusions

This work evaluated the thermal degradation kinetics for the membrane of pure cellulose acetate (AC-pure) and a series of hybrid cellulose acetate membranes, AC-SiO_2-$(CH_2)_3NH_2$, modified with the insertion of silicon and nitrogen from the precursors TEOS and APTES, respectively. The addition of silicon segment (A5-00) promoted the thermal stability of the membrane, presenting higher activation energy than the pure cellulose acetate membrane (AC-pure). The addition of nitrogen decreases the thermal stability compared to the cellulose acetate membrane with silicon (A5-00). However, it has more stability than the pure membrane. On the other hand, in membranes with higher nitrogen concentrations, especially the A5-50 membrane, there is a reduction in thermal stability, where the activation energy approaches the values of the pure membrane. Thus, with the present study of thermal degradation kinetics, it is possible to observe the influence of the chemical composition on the stability of the synthesized membranes and verify, especially, the effect of increasing the concentration of nitrogen in this regard. Despite a gain in mechanical properties and hydraulic permeability, the insertion of nitrogen through the APTES precursor must be carefully evaluated, considering the desired application for these new membranes. This profile was observed in all methods used in this study. However, it is noteworthy that the Friedman method is the most recommended method by the ICTAC, being a derivative method, which does not use mathematical approximations. In addition, it considers the loss of mass as a function of the conversion degree. Also, it uses the real heating rate in its calculations, which makes it the most reliable method among those evaluated.

Acknowledgments

The authors thank Prof. Dr. Clóvis Augusto Ribeiro for his enormous contribution. We also thank the financial support from FAPERJ, CAPES, and CNPq.

References

[1] N. M. José, L. A. S. A. Prado, “Hybrid organic-inorganic materials: preparation and some applications,” Química Nova, vol. 28, no. 2, pp. 281-288, 2005.

[2] M. C. Andrade, J. C. Pereira, N. de Almeida, P. Marques, M. Faria, M. C. Gonçalves, “Improving hydraulic permeability, mechanical properties, and chemical functionality of cellulose acetate-based membranes by co-polymerization with tetraethyl orthosilicate and 3-(aminopropyl)triethoxysilane,″ Carbohydrate Polymers, vol. 261, 2021. Available at: https://doi.org/10.1016/j.carbpol.2021.117813.

[3] G. Mendes, M. Faria, A. Carvalho, M. C. Gonçalves, M. N. de Pinho, “Structure of water in hybrid cellulose acetate-silica ultrafiltration membranes and permeation properties,” Carbohydrate Polymers, vol. 189, pp. 342-351, 2018. Available at: https://doi.org/10.1016/j.carbpol.2018.02.030.

[4] I. Peixoto, M. Faria, M.C. Gonçalves, “Synthesis and Characterization of Novel Integral Asymmetric Monophasic Cellulose–Acetate/Silica/Titania and Cellulose–Acetate/Titania Membranes,” Membranes, vol. 10, no. 9, 2020. Available at: https://doi.org/10.3390/membranes10090195.

[5] F. M. B. Coutinho, I. L. Mello, L. C. de Santa Maria, “Polyethylene: Main Types, Properties and Applications,” Polymers: Science and Technology, vol. 13, no. 1, pp. 1-13, 2003. Available at: https://doi.org/10.1590/S0104-14282003000100005.

[6] G. D. G. Mendes, “New Asymmetric Mixed Matrix Membranes of Cellulose and Silica Acetate,” Master's Dissertation, Post-Graduate Integrated Master's Program in Chemical Engineering, Instituto Superior Técnico de Lisboa, Lisbon, Portugal, 2016. Available at: https://fenix.tecnico.ulisboa.pt/cursos/meq/dissertacao/1691203502342679.

[7] V. M. K. da Rocha, “Study of The Degradation Kinetics of Polyester Resin From a Renewable Source,” Master's Dissertation, Postgraduate Program in Mining, Metallurgical and Materials Engineering, Federal University of Rio Grande do Sul, Porto Alegre, Brazil, 2018. Available at: https://lume.ufrgs.br/handle/10183/195760.

[8] S. Djalma, “Thermal Stability Study of Cellulose Acetate Propionate Modified With Short-Chain Polyhydroxyalkanes,” Master's Dissertation, Graduate Program in Engineering and Materials Science, State University of Norte Fluminense, Campos dos Goytacazes, Brazil, 2006. Available at: https://uenf.br/posgraduacao/engenharia-de-materiais/Mestrado-Djalma.pdf.

[9] I. C. de Miranda, “Study of The Kinetic Parameters of Thermal Decomposition of Lignocellulosic Residues And Characterization By Ta, Ftir And Edxrf,” Doctoral Thesis, Postgraduate Program in Chemical and Biochemical Process Technology, Federal University of Rio de Janeiro, Rio de Janeiro, 2013. Available at: http://epqb.eq.ufrj.br/wp-content/uploads/2021/10/d13_17.pdf.