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Effect of Rosemary Extract on the Thermal Stability of a Poly(ethylene oxide)-based Polymer Composite

M. Jakić,[*] J. Jakić, I. Krešić, and *M. Nikola Mužek*

University of Split, Faculty of Chemistry and Technology, Ruđera Boškovića 25, 21 000 Split,
Croatia

Abstract

The effect of rosemary extract (RE) addition on the thermal stability of poly(ethylene oxide) (PEO)-based composites was studied using thermogravimetric analysis (TG). Characteristic parameters of thermal degradation in an inert atmosphere were determined, and it was concluded that the addition of RE enhanced the thermal stability of the polymer matrix. Additionally, kinetic analysis was performed using isoconversional Flynn-Wall-Ozawa (FWO) and Friedman (FR) methods, as well as a multivariate non-linear regression method. The results revealed a three-stage thermal degradation process in all investigated samples, with the PEO degradation mechanism remaining unaffected by the presence of RE.

Keywords

Activation energy, kinetic analysis, poly(ethylene oxide), rosemary extract, thermogravimetric analysis

1 Introduction

Today, when the term "plastic" has become synonymous with waste generation, biodegradable composites have emerged as promising materials, especially for use in the packaging industry. In general, the main limitations of biodegradable polymers are their non-competitive production costs, and inadequate thermal and mechanical properties.[1] Polylactic acid (PLA) is an excellent example of a biodegradable, eco-friendly polymer that can be processed using conventional hot-melt processes. Despite its low cost and numerous advantages, PLA exhibits inferior mechanical properties, which limit its wider application.[2] Alternative base materials include poly(ethylene glycol) (PEG), and poly(ethylene oxide) (PEO), which are biocompatible, water-soluble polymers with significant industrial relevance – especially as carriers and coating agents in cosmetics and pharmaceuticals.[3] Conventional packaging must fulfil a range of critical functions, including protection and quality preservation; thus, biodegradable polymers are only part of the solution to the plastic waste problem. To develop new composite materials, synthetic additives must be replaced with natural alternatives. In this context, various natural extracts have been explored to improve the functionality of packaging materials or the packaged products themselves. Rosemary extract (RE) is an interesting natural additive, containing a phenolic structure comparable to synthetic antioxidants. It includes bioactive compounds such as carnosol, rosmaridiphenol, rosmadial, rosmarinic acid, and carnosic acid.[2,4] The incorporation of RE in active packaging systems has already been studied by numerous researchers.[5] However, the specific interaction between PEO (or PEG) and RE within polymer composites has not yet been thoroughly examined. Therefore, this study aimed to: (i) evaluate whether rosemary extract affects the thermal stability of PEO-based composites, and (ii) perform kinetic analysis to gain insight into the thermal degradation mechanisms of the investigated composites.

2 Experimental

2.1 Materials and preparation

Poly(ethylene oxide) (PEO; 100,000 g mol^{-1}, Sigma-Aldrich, Inc., St. Louis, USA) and rosemary extract (RE), derived from plant material purchased at Bio&Bio health food store Croatia), were used in this study. Samples of PEO/RE composites (99/1, 98/2, 95/5, 90/10) with varying RE mass fractions (1, 2, 5, and 10 wt%) were compounded using a twin-screw extruder (Haake MiniLab 3, Thermo Fischer, Waltham, USA) at 140 °C, and a screw speed of 100 rpm. The extruded samples used for further characterisation are shown in Fig. 1. Neat rosemary extract could not be processed in the twin-screw extruder. Therefore, an aqueous extract (15 g/100 ml), prepared in an ultrasonic bath (2 h at 60 °C), was lyophilised and used in powder form for analysis.

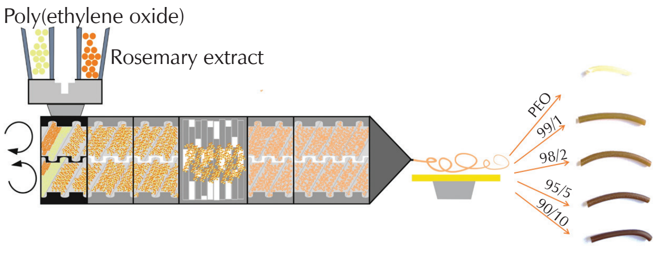

Fig. 1 – Extrusion of PEO/RE composite samples
Slika 1 – Ekstruzija uzoraka PEO/RE kompozita

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[*] Corresponding authors: Assoc. Prof. Mićе Jakić, PhD
Email: mice.jakic@ktf-split.hr
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2.2 Thermogravimetric analysis

Measurements were conducted using a PerkinElmer TGA 8000 instrument, over a temperature range from 30 °C to 600 °C, at five heating rates (5, 7.5, 10, 15, and 20 °C min^{-1}) in an inert nitrogen atmosphere (40 $\text{cm}^3\ \text{min}^{-1}$). The average sample mass was 7 mg. The following specific parameters were determined: onset temperature (T_{onset}), temperature at 5 % mass loss ($T_{5\%}$), temperature at the maximum degradation rate (T_{max}), maximum degradation rate (R_{max}), final mass (residue) (m_{f}), and mass loss (Δm).

2.3 Kinetic analysis

The kinetic analysis performed in this study is based on Eq. (1):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} \cong \beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\cdot\exp\left(-\frac{E}{RT}\right)\cdot f(\alpha) \tag{1}$$

where E is activation energy, A is Arrhenius pre-exponential factor, $f(\alpha)$ is kinetic model, α is the degree of conversion, β is the linear heating rate (K min^{-1}), T is the absolute temperature (K), R is the general gas constant (J $\text{mol}^{-1}\ \text{K}^{-1}$), and t is time (min). Before conducting a detailed kinetic analysis, the complexity of the process (dependence E *vs.* α), had to be examined using isoconversional methods. If E is independent of α, the process is considered simple, otherwise the process is complex and the shape of the E *vs.* α curve may suggest the possible reaction mechanism.[6] However, these methods do not provide data on A and $f(\alpha)$. Therefore, in this study, a model-fitting multivariate non-linear regression method, as part of the Netzsch Thermokinetic 3.1 software, was employed.

2.3.1. Isoconversional methods

Isoconversional methods calculate E values based on experimental α-T data ($\alpha = (m_0 - m)/(m_0 - m_{\text{f}})$), where m_0, m and m_{f} refer to the initial, actual, and residual mass of the sample obtained at several heating rates. In this study, the Friedman (FR) and Flynn-Wall-Ozawa (FWO) methods were used. FR (differential) method is based on Eq. (2).

$$\ln\left[\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right] = \ln A + \ln f(\alpha) - \frac{E}{RT} \tag{2}$$

FWO (integral) method is based on Eq. (3).

$$\log\beta = \log\frac{A\cdot E}{R\cdot g(\alpha)} - 2.315 - 0.4567\frac{E}{RT} \tag{3}$$

The experimental calculation and interpretation of the E *vs.* α dependence using FR ($\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)]$ *vs.* $1/T$) and FWO plots ($\log\beta$ *vs.* $1/T$), as well as the tips for performing kinetic analysis using Netzsch software, are detailed in our previously published articles.[3,7–9]

3 Results and discussion

3.1 Thermogravimetric analysis

To evaluate the influence of RE addition on the thermal stability of PEO, TG/DTG characteristics (derived from the curves in Fig. 2) are presented in Table 1. Neat PEO undergoes two stages of degradation. The first stage is attributed to moisture loss, beginning at 64 °C (T_{onset1}) with a T_{max1} at 77 °C, leaving a residue of 99.2 %. This observation is contrary to our earlier findings,[7–11] where neat PEO was shown to thermally decompose in a single primary degradation stage. However, this moisture can be verified by Fourier transform infrared spectroscopy (FT-IR). In our earlier work,[12] FT-IR was utilised to determine whether RE addition affects the structural properties of PEO. Broad bands in the range of 3400–3500 cm^{-1} were observed in all PEO/RE composites, as shown in Fig. 3. The complete FT-IR spectra are available in our previously published work.[12] According to *Alsabagh et al.*[13] and *Brogly et al.*[14], these bands correspond to OH stretching (H_2O). Therefore, the aforementioned mass loss can be attributed to the evaporation of physically adsorbed and fractionally hydrogen-bonded

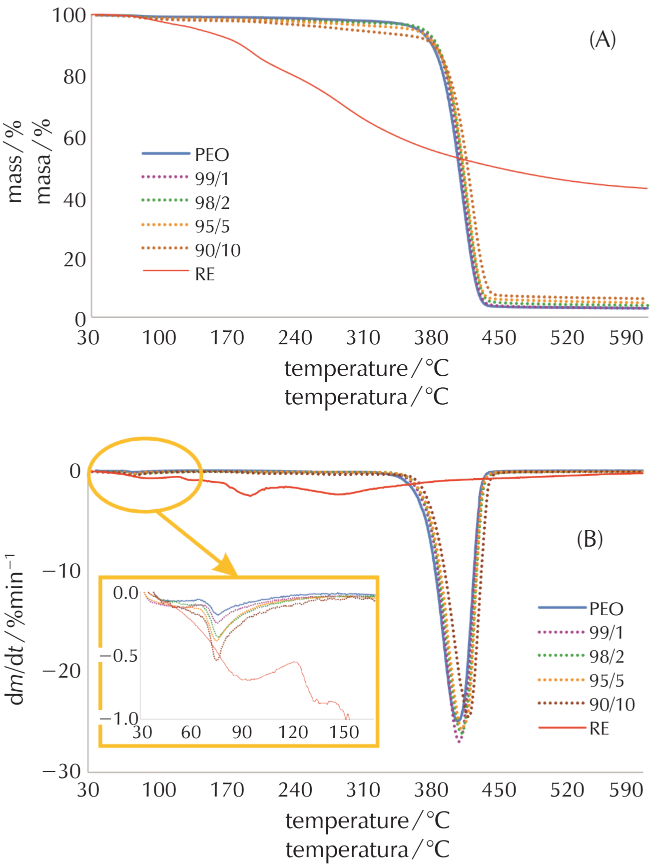

Fig. 2 – TG (A) and corresponding DTG (B) curves of the thermal degradation of the PEO/RE composite samples (heating rate 10 °C min^{-1})

Slika 2 – TG (A) i DTG (B) krivulje toplinske razgradnje uzoraka PEO/RE kompozita (brzina zagrijavanja 10 °C min^{-1})

Table 1 – Parameters from TG/DTG curves of PEO/RE composites (heating rate 10 °C min^{-1})
Tablica 1 – Značajke određene iz TG/DTG krivulja PEO/RE kompozita (brzina zagrijavanja 10 °C min^{-1})

Parameter / Značajka →	$T_{5\%}$ / °C	T_{onset} / °C	T_{max} / °C	R_{max} / %min^{-1}	Δm / %	m_{f} / %
Sample / Uzorak↓	1st degradation stage / 1. stupanj razgradnje					
PEO	365	64	77	0.2	0.8	99.2
99/1	370	57	76	0.2	1.1	98.9
98/2	371	66	77	0.4	1.3	98.7
95/5	362	62	76	0.4	1.4	98.6
90/10	300	65	76	0.5	1.8	98.2
RE	140	67	91	0.7	3.7	96.3
Sample / Uzorak↓	2nd degradation stage / 2. stupanj razgradnje					
PEO	–	386	409	24.9	96.4	2.8
99/1	–	389	411	26.9	95.8	3.2
98/2	–	392	413	26.2	94.8	3.9
95/5	–	391	414	25.7	93.9	4.8
90/10	–	395	421	24.4	92.0	6.3
RE*	–	170/261*	196/287*	2.4/2.3*	15.8/37.8*	80.5/42.6*

*neat RE degrades through three degradation stages
*čisti RE razgrađuje se kroz tri razgradna stupnja

water.[14] The second degradation stage of neat PEO begins at 386 °C and peaks sharply at 409 °C, leaving a residue of 2.8 %. This main degradation stage proceeds via random chain scission of C–O bonds,[15] where the ethyl alcohol, methyl alcohol, alkenes, non-cyclic ethers, formaldehyde, acetic aldehyde, ethylene oxide, water, CO, and CO$_2$ are the main decomposition products.[16]

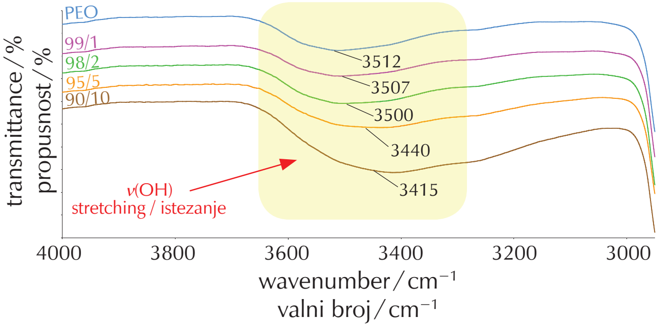

Fig. 3 – FT-IR spectra of neat PEO and PEO/RE composite samples in the stretching region of interest
Slika 3 – FT-IR spektri čistog PEO i uzoraka PEO/RE kompozita u području istezanja od interesa

Contrary to PEO, within the same temperature range, the thermal decomposition of RE powder revealed three main stages. The first stage, occurring at 67 °C (T_{onset1}) and peaking at 91 °C (T_{max1}), and the second stage, at 170 °C (T_{onset2}) and 196 °C (T_{max2}), can be attributed to the evaporation of bound water, volatile phenolic compounds, and solvent. The overall mass loss of 19.5 % is notably higher than values reported in the literature (0.5–6 %).[17,18] It should be emphasised, however, that in this study the RE was not extruded (at 140 °C); rather, the powder used was obtained from the aqueous extract. The third stage resulted in a major mass loss of 37.8 %, corresponding to a DTG peak observed at 287 °C (Figure 2B), which can be ascribed to the evaporation of volatile compounds originating from phenolic diterpenes.[17,18] The final mass at 600 °C was relatively high (42.6 %), indicating the presence of the most thermally stable components.

The thermal degradation of PEO/RE composite samples follows a two-stage pattern similar to that of neat PEO, as shown by the two peaks on the DTG curves (Fig. 2B). The first stage corresponds to the evaporation of physically adsorbed water, while the second degradation stage aligns fully with the main degradation stage of neat PEO. Based on the parameters in Table 1, the effect of RE on the thermal stability of PEO can be assessed. Regarding the mass loss (Δm) during the first degradation stage, an increase of approximately 1% was observed upon RE addition. This is an indication that, apart from the physically adsorbed water, some volatile phenolic compounds from the extract incorporated into the PEO matrix are also evaporating. However, the key parameters (T_{onset1} and T_{max1}) for the composite samples in the first stage remain practically independent upon RE addition. Therefore, the focus shifts to the main, second degradation stage. Upon addition of 1 wt.% of RE, parameters T_{onset2} and T_{max2}, increased by 3°C and 2 °C, respectively. At the highest RE concentration, the total increment was 9 °C and 11 °C, respectively. This is clear evidence of RE's stabilising effect on PEO. Although no literature on thermal degradation of the PEO(PEG)/RE composites is available, comparisons with other polymer/RE systems are insightful. *Darie-Nita et al.*[2] investigated PLA/PEG/RE-based materials and found that, while PLA/RE samples decomposed in a single stage, revealing a lower thermal stability compared to neat PLA, the addition of RE actually enhanced the thermal stability of the PLA/PEG material. Similarly, *Vasile et al.*[1] reported enhanced thermal stability of PLA/PEG/RE materials with incorporated RE.

3.2 Kinetic analysis

PEO and its composites have previously been studied by our research group.[3,7–9,19] In general, PEO decomposes via a mechanism involving consecutive reactions. The main reaction models that have shown good theoretical agreement include the Avrami-Erofeev (An) model and the n^{th}-order reaction with autocatalysis (Cn).

However, kinetic data specific to RE are scarce. To our knowledge, only a few studies have explored its kinetics: these include investigations of antioxidant properties,[20] determination of the most suitable model and extraction parameters for the active compounds from RE[21–24] , and evaluation of the degradation kinetics in Choibá oil supplemented with RE using a linearised Arrhenius model.[25] In the latter, oxidative stability and shelf life were assessed through peroxide value measurements, with results suggesting that the addition of RE increases the oxidative stability of Choibá oil.

In this study, emphasis was placed on PEO/RE composite samples. The apparent activation energies for the thermal degradation of the investigated samples were determined using FR and FWO plots (Figs. 4 and 5 respectively).

In Fig. 6, it is evident that, for all composite samples, *E* depends on α. Three distinct regions clearly indicate a three-stage degradation process. Therefore, the process is classified as complex, and a detailed analysis was conducted for each individual stage. The results are presented in Table 2.

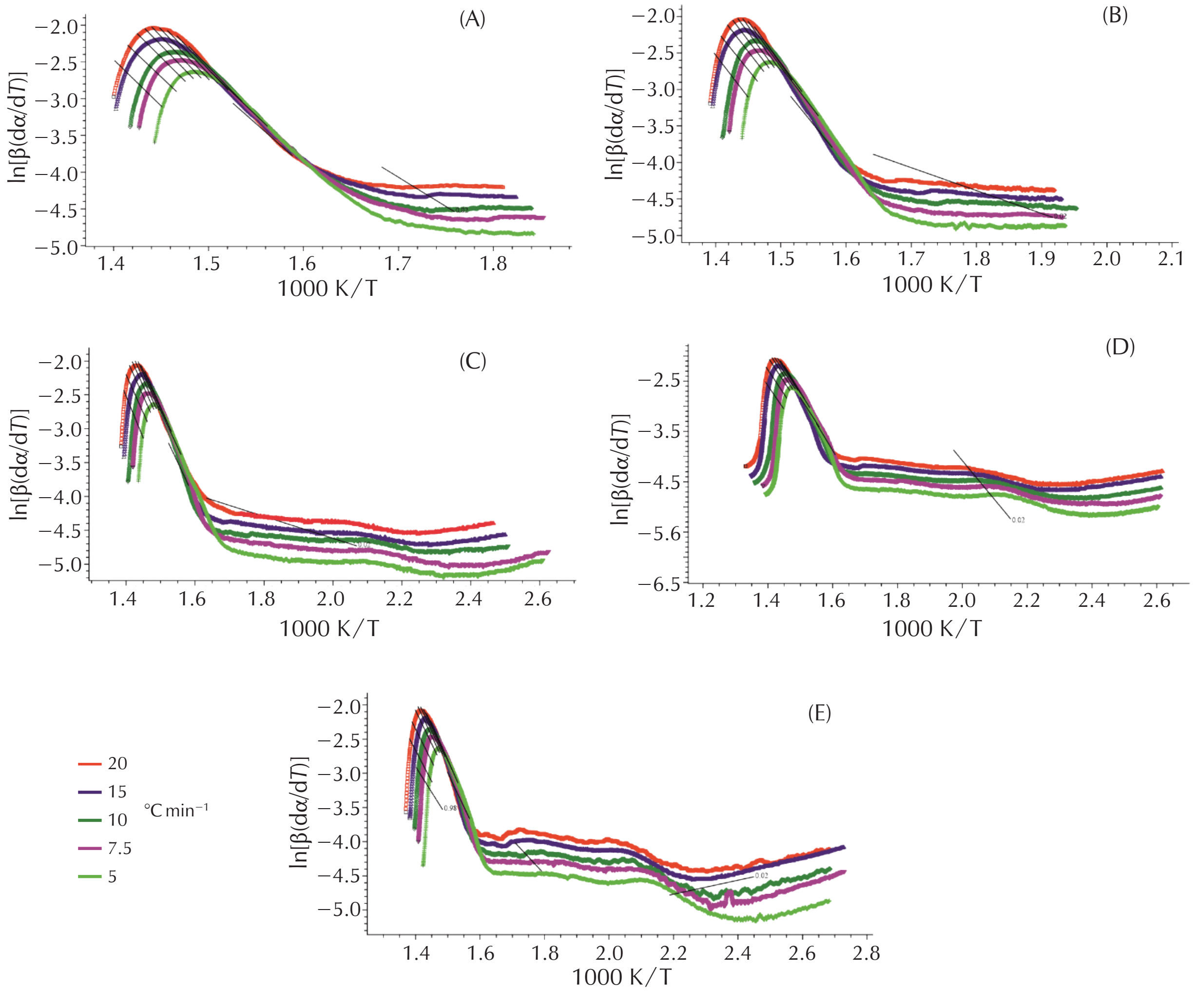

Fig. 4 – Friedman plots: (A) PEO, (B) 99/1, (C) 98/2, (D) 95/5, and (E) 90/10
Slika 4 – Izokonverzijski pravci prema FR metodi: (A) PEO, (B) 99/1, (C) 98/2, (D) 95/5 i (E) 90/10

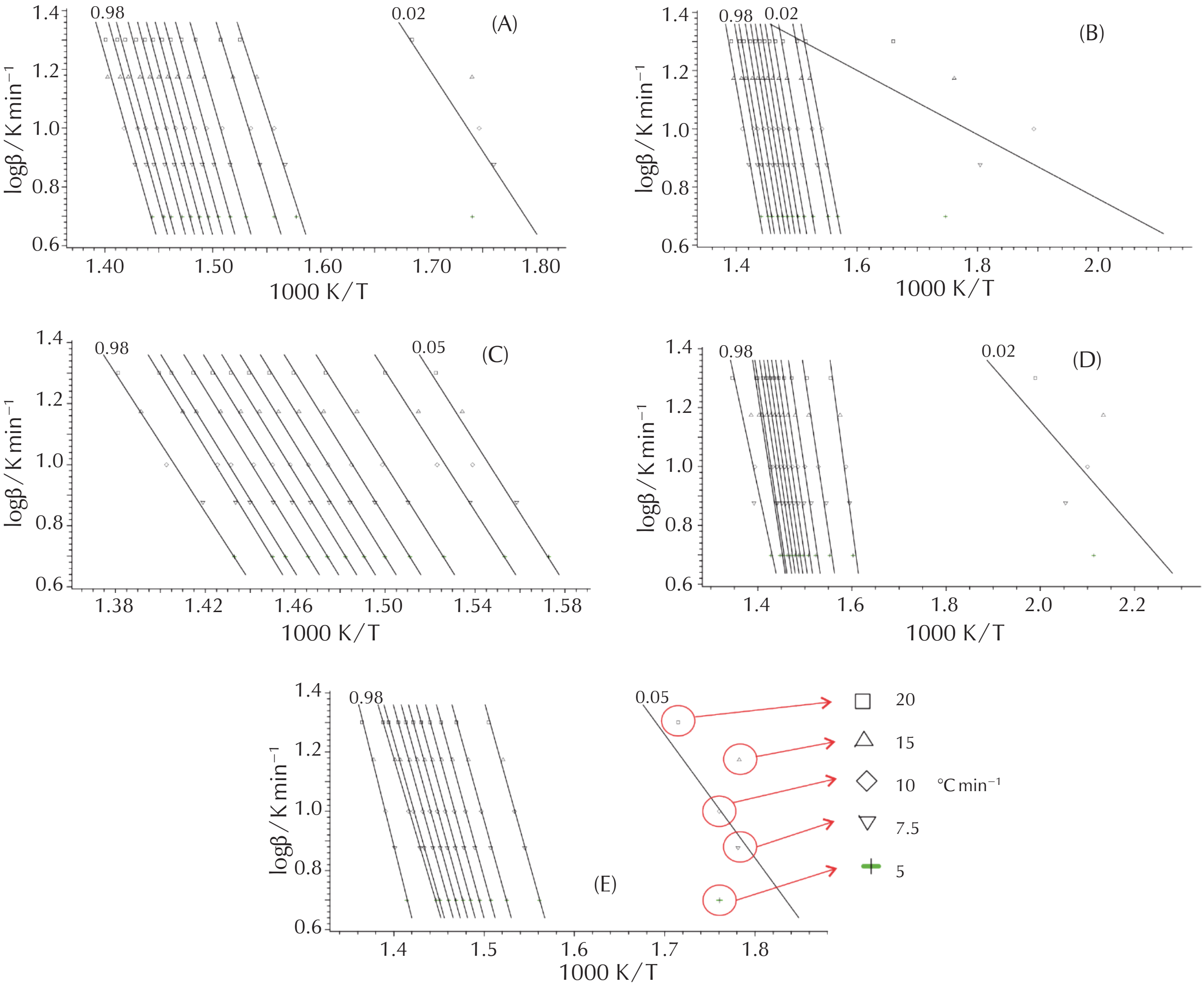

Fig. 5 – Flynn-Wall-Ozawa plots: (A) PEO, (B) 99/1, (C) 98/2, (D) 95/5, and (E) 90/10
Slika 5 – Izokonverzijski pravci prema FWO metodi: (A) PEO, (B) 99/1, (C) 98/2, (D) 95/5 i (E) 90/10

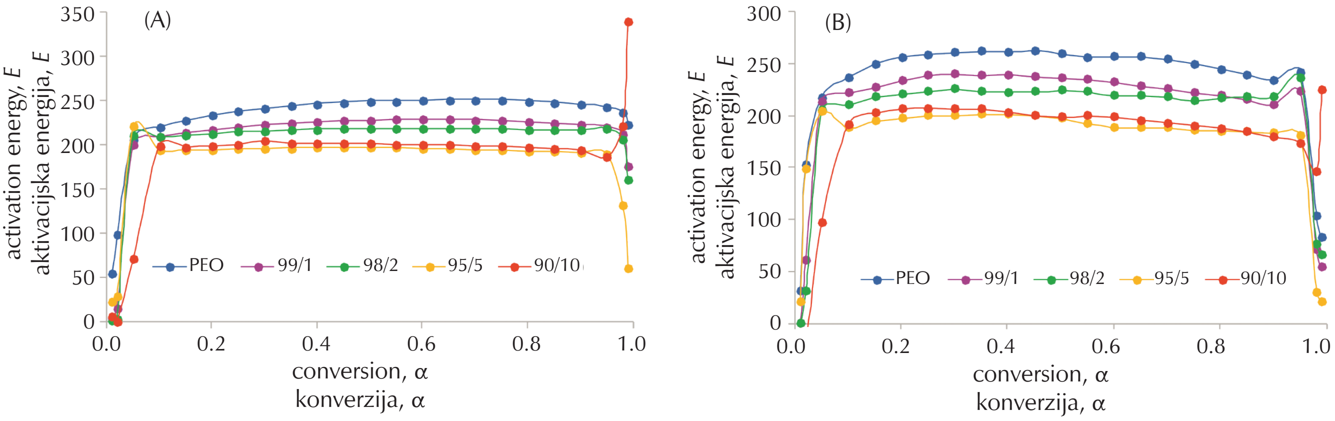

Fig. 6 – *E vs.* α for neat PEO and composite samples: (A) FWO, (B) FR
Slika 6 – *E vs.* α za čisti PEO i uzorke kompozita: (A) FWO, (B) FR

Table 2 – Kinetic parameter values calculated using Thermokinetics software
Tablica 2 – Kinetički parametri izračunati primjenom Thermokinetics softvera

Stage of reaction	Parameter	PEO/RE				
		PEO	99/1	98/2	95/5	90/10
Stage I	E_1 / kJ mol^{-1}	45.7	61.4	32.2	31.4	37.9
	logA_1	1.1	4.2	0.2	0.1	0.4
	n	–	–	–	–	–
	Model	D3	D3	D3	D3	D3
FR	kJ mol^{-1}	30.8–217.3	61.2–213.5	30.9–204.7	21.3–203.6	0.0–191.3
FWO	kJ mol^{-1}	55.0–219.8	4.8–239.6	3.7–211.6	23.5–221.8	5.9–199.4
Stage II	E_2 / kJ mol^{-1}	246.3	221.2	215.9	200.8	205.1
	logA_2	16.7	14.6	14.1	12.9	13.2
	n	0.9	0.8	0.7	1.1	0.6
	Model	Cn	Cn	Cn	Cn	Cn
FR	kJ mol^{-1}	233.8–262.1	221.8–239.6	214.5–225.3	185.2–201.2	184.1–206.9
FWO	kJ mol^{-1}	227.5–250.9	208.9–228.8	213.2–219.2	191.1–197.5	186.7–202.0
Stage III	E_3 / kJ mol^{-1}	102.8	69.1	135.7	174.6	222.8
	logA_3	7.6	0.6	10.4	9.5	17.5
	n	3.1	3.6	3.5	2.7	4.3
	Model	Fn	Fn	Fn	Fn	Fn
FR	kJ mol^{-1}	82.5–102.8	53.8–70.7	66.3–236.2	21.4–180.4	145.3–224.14
FWO	kJ mol^{-1}	223.6–236.8	176.2–212.0	161.2–206.8	61.2–189.8	222.2–339.4
Coefficient of determination, r^2		0.99995	0.99990	0.99996	0.99981	0.99992

The three-stage degradation mechanism (consecutive reactions) for all samples, as shown in Fig. 7, is validated with an $r^2 > 0.9999$. The first stage corresponds to the evaporation of physically adsorbed and fractionally hydrogen-bonded water, as confirmed by the TG results. This mass loss is best described by a three-dimensional diffusion model of the Jander type (D3). Further details on diffusion-based kinetic models and guidance on initiating such analyses can be found in the literature.[3,7,8]

The second stage of all samples is characterised by the same model: Cn. Therefore, it can be concluded that the addition of RE did not alter the decomposition mechanism of PEO. The same applies to the final, third degradation stage, which follows the Fn reaction model for all investigated samples. However, the observed decreasing trend in *E* values (Table 2) may indicate a deterioration in thermal stability. This is contrary to the conclusion drawn from the TG analysis. Nevertheless, this apparent contradiction could be deceptive. It is important to note that degradation is recorded as mass loss of the volatile compounds from PEO or RE, respectively. Therefore, interaction of volatiles and PEO or RE can occur and alter the diffusion (evaporation) process from the sample.

4 Conclusion

In this study, the effect of rosemary extract on the thermal stability and kinetic degradation scheme of PEO was investigated. Thermogravimetric analysis indicated a stabilising effect of RE on the PEO matrix. Kinetic analysis revealed that all samples decomposed via a three-stage mechanism. In the beginning of decomposition, the diffusion of physically bonded water was the dominant reaction process for all samples. In the main degradation stage, all composite samples followed the same reaction model, indicating that rosemary extract had no effect on the thermal degradation mechanism of PEO.

ACKNOWLEDGEMENTS

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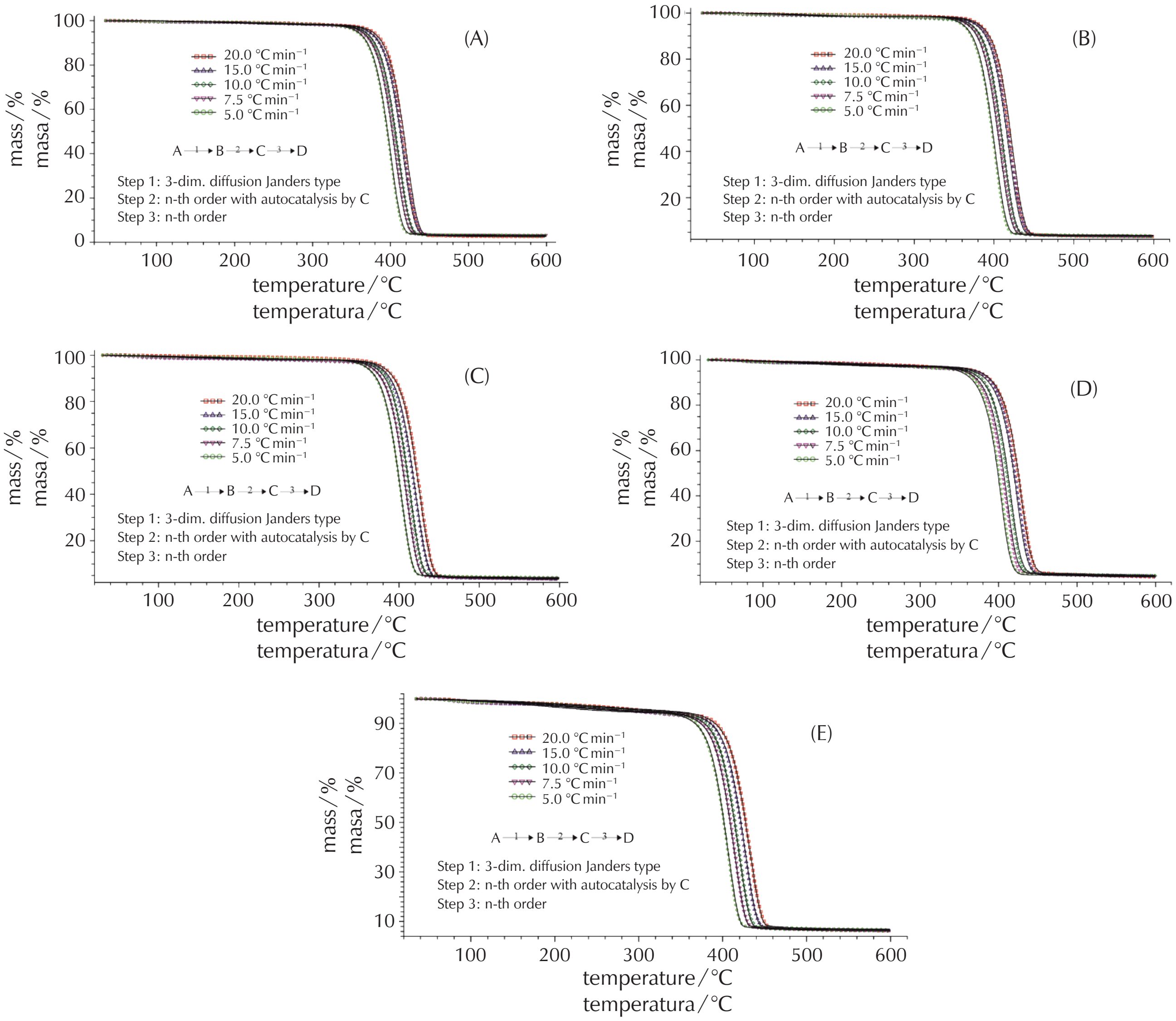

Fig. 7 – Selected kinetic models (solid) fitted to experimental data (points): (A) PEO, (B) 99/1, (C) 98/2, (D) 95/5, and (E) 90/10

Slika 7 – Prikaz odabranih kinetičkih modela (linija) uspoređenih s eksperimentalnim podatcima (točke): (A) PEO, (B) 99/1, (C) 98/2, (D) 95/5 i (E) 90/10

List of symbols and abbreviations
Popis simbola i kratica

FT-IR – Fourier transform infrared spectroscopy
– infracrvena spektroskopija s Fourierovom transformacijom

DSC – differential scanning calorimetry
– diferencijalna pretražna kalorimetrija

TG – thermogravimetric analysis
– termogravimetrijska analiza

T_{onset} – onset temperature
– temperatura početka razgradnje

$T_{5\%}$ – temperature at 5 % mass loss
– temperatura pri kojoj uzorak izgubi 5 % početne mase

$T_{\max}$ – temperature at the maximum degradation rate
– temperatura pri maksimalnoj brzini razgradnje

$R_{\max}$ – maximum degradation rate
– maksimalna brzina razgradnje

m_{f} – final mass
– konačna ostatna masa

Δm – mass loss
– gubitak mase za pojedini stupanj razgradnje

E – activation energy
– aktivacijska energija

A – Arrhenius pre-exponential factor
– Arrheniusov predeksponencijalni faktor

$f(\alpha)$ – kinetic model
– kinetički model

α – degree of conversion
– stupanj konverzije

β – linear heating rate
– brzina zagrijavanja

T	– absolute temperature – apsolutna temperatura
R	– general gas constant – opća plinska konstanta
t	– time – vrijeme
FR	– Friedman
FWO	– Flynn-Wall-Ozawa

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SAŽETAK

Utjecaj ekstrakta ružmarina na toplinsku stabilnost polimernog kompozita na bazi poli(etilen-oksida)

Miće Jakić,[*] *Jelena Jakić*, *Irena Krešić* i *Mario Nikola Mužek*

Istraživan je utjecaj dodatka ekstrakta ružmarina (RE) na toplinsku stabilnost polimernog kompozita na bazi poli(etilen-oksida) (PEO) primjenom termogravimetrijske analize (TG). Određeni su karakteristični parametri toplinske razgradnje kompozita u inertnoj atmosferi te se može zaključiti da dodatak ekstrakta poboljšava toplinsku stabilnost polimerne matrice. Također, provedena je kinetička analiza primjenom izokonverzijske Flynn-Wall-Ozawa (FWO) i Friedman (FR), kao i nelinearna regresijska metoda analize. Zaključeno je da se toplinska razgradnja svih uzoraka kompozita odvija kroz tri stupnja, gdje dodatak ekstrakta nije utjecao na mehanizam razgradnje poli(etilen-oksida).

Ključne riječi
Aktivacijska energija, kinetička analiza, poli(etilen-oksid), ekstrakt ružmarina, termogravimetrijska analiza

Sveučilište u Splitu, Kemijsko-tehnološki fakultet, Ruđera Boškovića 25, 21 000 Split

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