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IMPACT OF THE ROSEMARY EXTRACT ON THE THERMAL STABILITY OF THE POLY(ETHYLENE OXIDE) POLYMER BASED COMPOSITE

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INTRODUCTION

During the last decades, in order to reduce plastic waste generation, great efforts have been made to explore new bio-based packaging materials. Since they must have important functions, similar to conventional packaging, including containment and protection of product and maintaining of its quality and safety, these materials alone may only partially solve the waste problem. The interesting base materials are poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO). PEO is known as semicrystalline, biocompatible, biodegradable, non-ionic and water-soluble polymer of considerable industrial significance which finds applications in many different branches of industry. Likewise, PEG is used as lubricant, intermediate, binder, solvent, carrier and coating in the cosmetic, pharmaceutical, paper, food, textile and chemical specialty fields. In order to develop the new multifunctional materials as a key for new active materials strategies, instead of the synthetic ones, natural additives must be used. Hence, different natural extracts have been proposed for incorporation into the polymer matrices to improve the functionality as well as the products (food and pharmaceuticals) quality and safety. A phenolic structure pattern similar to that of synthetic antioxidants can be found in the constituents of rosemary leaves and their extracts. Hence, the main goal of this work is to investigate the effect of the rosemary extract (RE) on the thermal stability of the PEO matrix by thermogravimetric analysis. Likewise, the complexity of the degradation process was investigated by determining the dependence of activation energy on conversion by isoconversional Friedman and Flynn-Wall-Ozawa method incorporated in the Netzsch Thermokinetics 3.1 software.

Table 1. The characteristics of thermal degradation curves of PEO/RE composites at 10 °Cmin^{-1}.

Parameter →	$T_{5\%}$ (°C)	T_{onset} (°C)	T_{max} (°C)	R_{max} (%min^{-1})	Δm (%)	m_f (%)
Sample↓	1° degradation stage					
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↓	2° degradation stage					
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

*RE degrades through three degradation stages.

EXPERIMENTAL PART

Materials and preparation

Materials used in this work are as follows: poly(ethylene oxide) (PEO), 100,000 gmol^{-1}, Sigma-Aldrich, Inc., St. Louis, USA; and rosemary extract, RE (plant material, Bio&Bio, Croatia). The PEO/RE composites of different mass fraction of extract (1, 2, 5 and 10 wt %) were prepared via hot melt extrusion in a laboratory twin screw extruder (Haake MiniLab 3, Thermo Fischer, Waltham, USA), Fig. 1. Rosemary extract particles couldn't be extruded in abovementioned extruder. Hence, aqueous extract (15 g/100 mL) prepared using an ultrasonic bath (2 h at 60 °C) were lyophilized and were used for the analysis as powder.

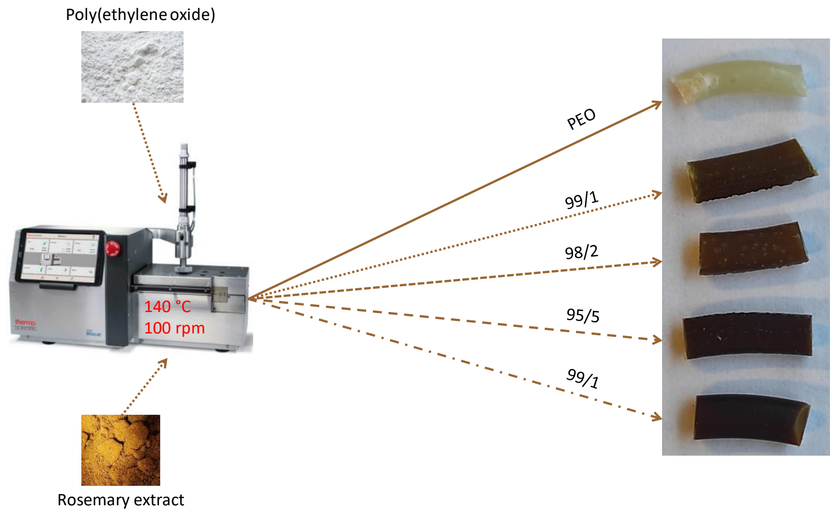

Fig. 1. Preparation process of the PEO/RE composite samples

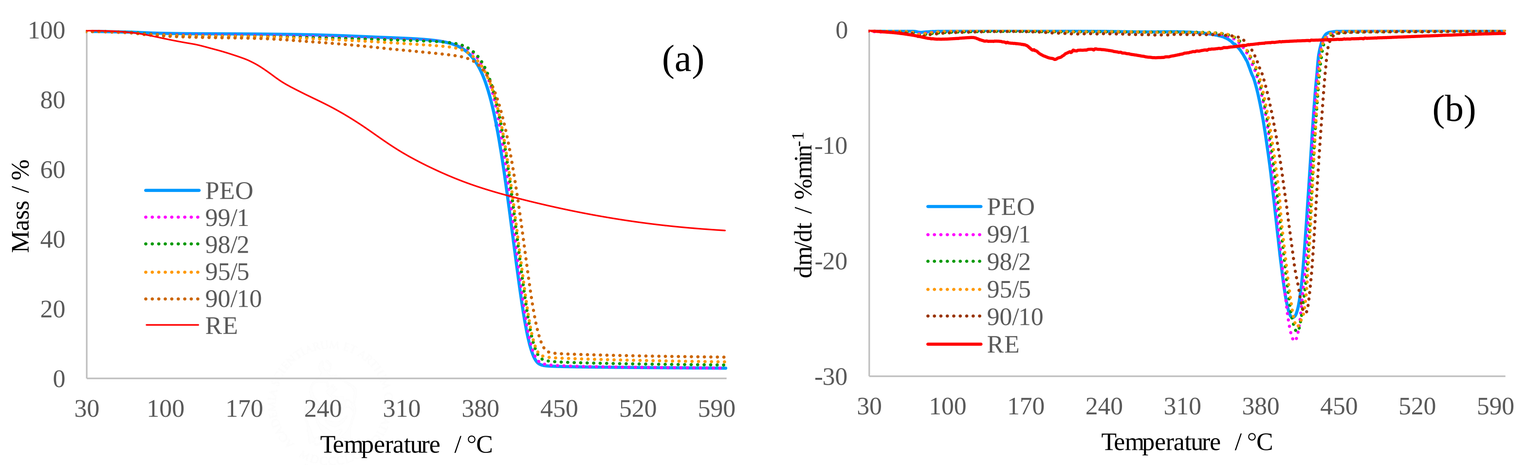

Fig. 2. TG (a) and DTG (b) curves of the thermal degradation of the PEO/RE composites at the heating rate of 10 °Cmin^{-1}.

Method and calculation

Thermogravimetric measurements were conducted by using PerkinElmer TGA 8000 at the different heating rates (5, 7.5, 10, 15 and 20 °Cmin^{-1}) in a temperature range 30-600 °C under a steady flow of nitrogen (40 cm^{3}min^{-1}). Samples weighing approximately 7 mg for the analysis were used. To evaluate the thermal stability of the investigated samples the following characteristics were determined: the onset temperature (T_{onset}), the temperature at 5% mass loss ($T_{5\%}$), the temperature at the maximum degradation rate (T_{max}), the maximum degradation rate (R_{max}), the final mass (m_f) and the mass loss (Δm) for the corresponding degradation steps. Furthermore, Ea values and Ea vs. α dependence have been calculated by means of isoconversional integral Flynn-Wall-Ozawa (FWO) and differential Friedman (FR) methods (Fig. 3).

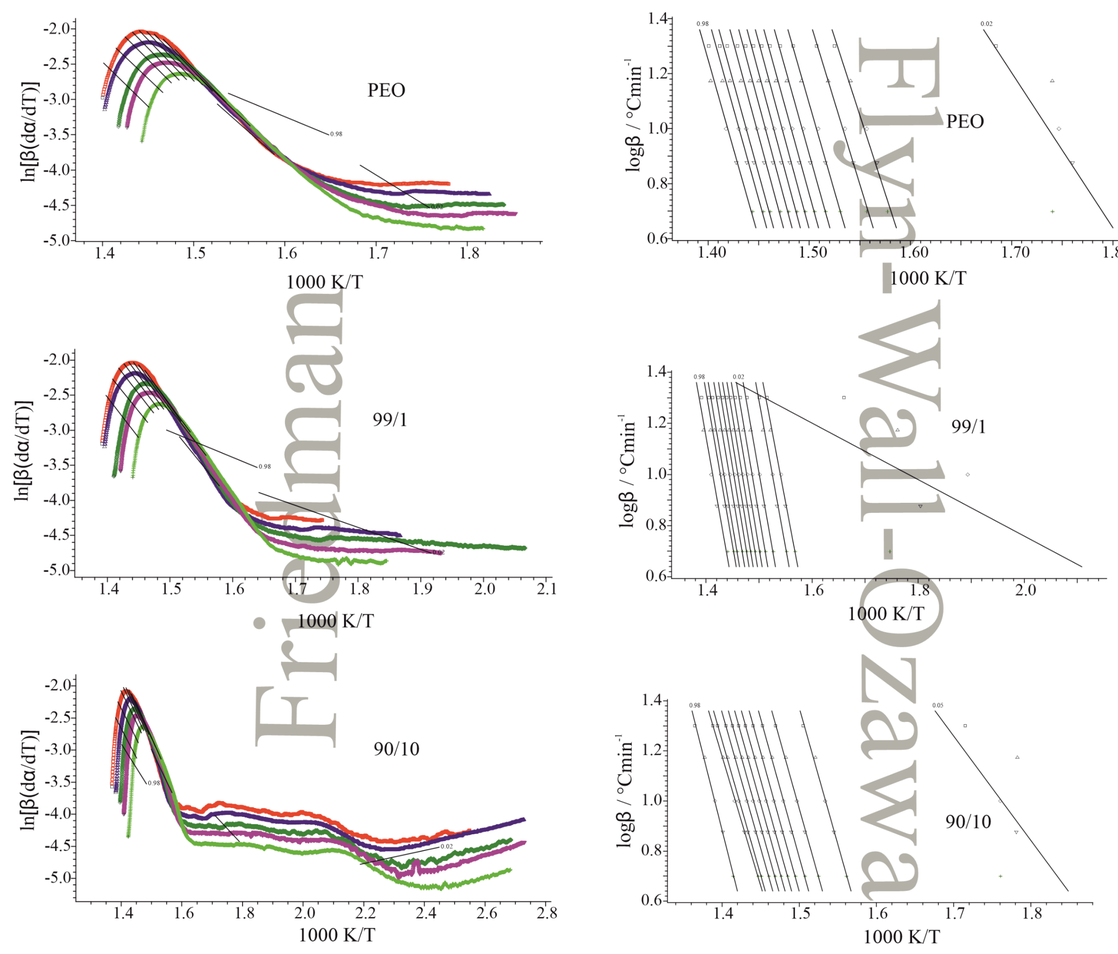

Fig. 3. Flyn-Wall-Ozawa and Friedman plots for the thermal degradation of the selected samples.

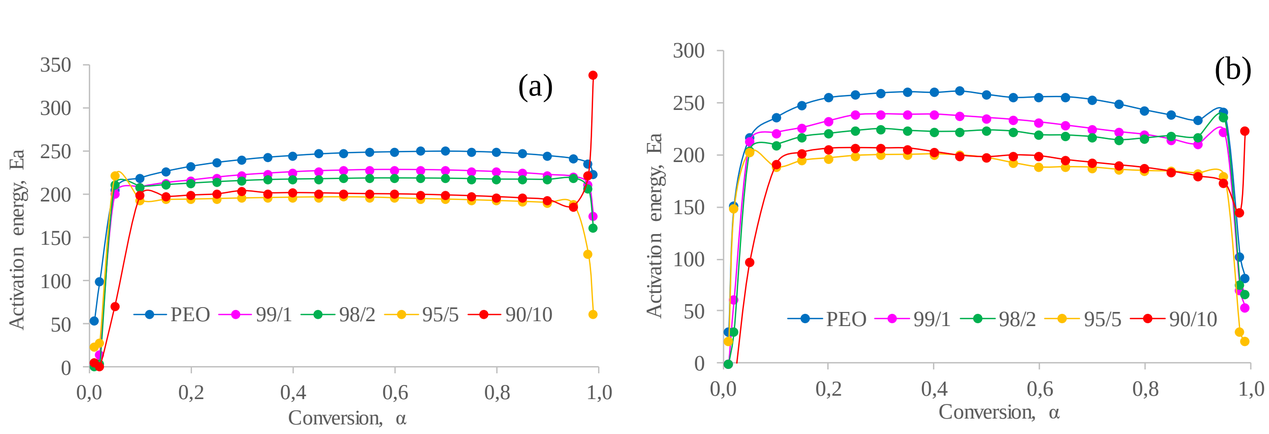

Fig. 4. Activation energy as a function of degree of conversion for PEO/RE composites calculated by
means of Flyn-Wall-Ozawa (a) and Friedman method (b).

Conclusions

The degradation of all PEO/RE samples is found to follow similar pattern as neat PEO and shows two-stage degradation (Fig. 2). First stage correspond to the moisture loss, while the second one is the main degradation stage. From these data it could be concluded that the degradation of composite samples starts at higher temperatures (Table 1). Finally, this results could be an indication of rosemary extract stabilising effect on the PEO matrix.

Prior to any kinetic analysis one should investigate the complexity of the process by determining the dependence of Ea on α. It can be concluded from Fig. 4 that ER addition did not affect the degradation mechanism of the PEO. In order to confirm this conclusion, further kinetic analysis is needed.

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