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Microcalorimetric Characterization of Polymer Composites Biodegradability †

Adina Magdalena Musuc [1,*], Mihaela Doni [2] and Vlad Tudor Popa [1]

1 Romanian Academy, "Ilie Murgulescu" Institute of Physical Chemistry, 202 Spl. Independentei, 060021 Bucharest, Romania; vtpopa@icf.ro
2 National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, 202 Spl. Independentei, 060021 Bucharest, Romania; mihaela.doni@icechim.ro
* Correspondence: amusuc@icf.ro
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Abstract: Nowadays, one of the major environmental risks is the slow rate of plastic materials degradation or even the non-biodegradability of some organic compounds in real life systems. Therefore, green additives and adequate processing of the packaging materials are needed to intensify the plastic biodegradation under natural conditions. In this work, commercial grade low-density polyethylene (LDPE) with 1% rosemary (*Rosmarinus officinalis L.*) extract was used for the preparation of composite films. The biodegradability studies were carried out by incubating the unmodified and modified composites with *Aspergillus Niger*. Based on microcalorimetric results it can be concluded that rosemary extract can be used for increasing the biodegradability of polyethylene films *via* reducing of its crystallinity degree.

Keywords: microcalorimetry; biodegradability; crystallization.

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1. Introduction

The present production and global consumption of plastics (especially for packaging) is continuously increasing, leading to an inefficient waste management system. In order to reduce the waste products, the plastic materials decrease, recycling and alternative use of environmentally friendly materials must be considered. Plastic packaging materials represent a large percentage of the materials used for food packaging. Because most of them are not biodegradable, a constant challenge for packaging material technologists is to design environmentally friendly systems containing biodegradable materials.

One of the major environmental threats is the slow rate of degradation or non-biodegradability of the organic materials under natural conditions. Recently, research was focused on the use of bio-based materials made from organic, natural, or renewable resources for manufacturing food package [1–4]. Another way to increase the biodegradability of food packaging is the incorporation in plastic materials of essential oils extracted from plants which yields composites with enhanced biodegradability characteristics [5,6]. Essential oils from plants and spices have been extensively studied as materials used for incorporation into the film microstructure due to their influence on: (i) physical (tensile, optical) and structural properties of the plastic materials; (ii) antioxidant power and (iii) antimicrobial effects [7,8].

Polyethylene is present in many applications in daily use because of its easy processing and its low cost. It is used for carrying food articles, for packaging textiles, for manufacturing laboratory instruments and automotive components. Rosemary (*Rosmarinus officinalis L.*) is a medicinal and culinary herb well-known for its potential health benefits, such as antibacterial, antioxidant and anti-inflammatory. Many studies have demonstrated that the incorporation of the rosemary essential oils into food packaging can improve the antioxidant properties of packaging materials [9,10]. During the last years, scientific research groups have studied the biodegradation of polyethylene. Thermal analysis techniques are adequate to assess the thermal properties and the effect of biodegradation on the structure of biodegradable biopolymers.

This contribution is therefore dedicated to the study of thermal behavior of low-density polyethylene films with 1% rosemary content using microcalorimetry technique, at different heating rates. The biodegradability studies were carried out by incubating the modified low density polyethylene films with *Aspergillus Niger*. The incorporation of rosemary extract in polyethylene films was proven to enhance their biodegradability *via* reducing of the crystallinity degree.

2. Materials and Methods

2.1. Materials

Commercial grade low-density polyethylene (LDPE) was provided by Sigma (Germany) and used as received. The other reagents used in the experiments were purchased as follows: D(+)-glucose from Loba (Austria), peptone from Oxoid (UK) and rosemary extract powder (RM) from S.C. Hofigal S.A. (Romania). They were used without further purification. *Aspergillus Niger* was provided from Microbial Collection of INCDCP–ICECHIM.

2.2. Preparation of LDPE films with 1% RM extract

Low-density polyethylene films with a concentration of 1% rosemary extract (LDPE 1% RM) were prepared by mixing in molten state LDPE and RM using a Brabender Plastograph. Subsequently, the extrusion–calendering process was performed successfully to produce composite films with thickness of 0.6 mm. The composite films were cut into pieces of 2 cm x 2 cm. The polymer films were extruded at 190^{o}C, at a screw speed sheet extrusion of 40 rpm. For comparison, a blank sample (noted LDPE) with 0% rosemary extract was used.

2.3. Microbial attack

The polyethylene with 1% rosemary composite films were exposed to the microorganism (*Aspergillus Niger*) contact during liquid cultivation in Sabouraud diluted medium (1 % peptone; 2.2 % D(+)-glucose). The films were sterilized for 10 min at UV light. Then, each piece was aseptically transferred and placed into sterile medium. The culture was carried out in orbital incubator Heidolph Unimax 1000 at 200 rpm and 37 ± 2^{o}C, for 50 days, in 100 mL Erlenmeyer flasks which contained 50 mL of the highly nutritive liqiud medium. A blank sample (noted Control sample) was prepared by introducing in 50 mL medium without microbial inoculation. The control sample was also maintained in identical conditions as the samples with *Aspergillus Niger* inoculation. The samples were analyzed in triplicate.

2.4. Methods

The thermal runs were performed on a SETARAM microDSC 7 evo differential scanning calorimeter within the 50–120^{o}C temperature range, at heating rates of 0.2, 0.3, 0.4, 0.6 and 1^{o}C min^{-1}, in nitrogen atmosphere with a flow rate of 50 mL min^{-1}. Sample mass was of 1 mg. Microcalorimetric curves (μDSC) were further used for obtaining the physical and thermal parameters of studied samples.

3. Results and Discussion

μDSC measurements were used for the estimation of melting temperature (T_m) (as the minimum of endothermal peak) and the corresponding melting heat (ΔH_m) (as endothermal peak area) of polyethylene films. The crystallinity degree (c%) was calculated according to equation (1):

$$c\% = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \qquad (1)$$

where ΔH_m^0 is the melting enthalpy of a perfectly crystalline polyethylene (293 J/g) [11].

In Figure 1 were represented the µDSC curves of the raw LDPE (Figure 1a) and LDPE incorporated with 1% RM extract (Figure 1b). The results show that the presence of the 1% rosemary extract affects the shape of the curves. The samples which contain rosemary extract exhibit a broader endothermal peak compared with raw polyethylene for all used heating rates.

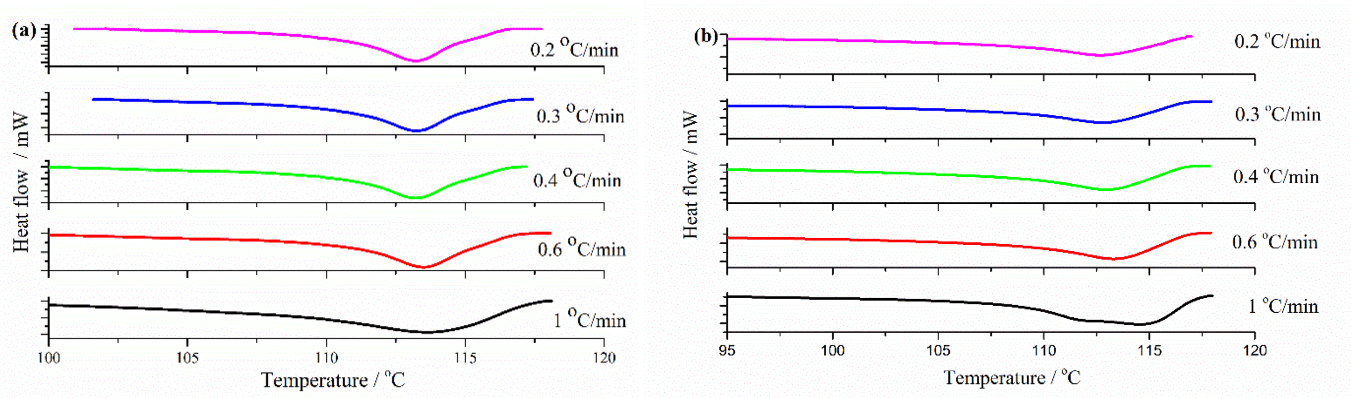

Figure 1. µDSC melting curves of (a) LDPE and (b) LDPE with 1% rosemary at several heating rates, in nitrogen atmosphere.

The melting endotherm of raw polyethylene (LDPE) exhibits a peak temperature of ~113.2°C. The incorporation of 1% rosemary extract in the LDPE films (Figure 3b) affects the peak melting temperatures which shows a slight decrease. In the µDSC curve of LDPE with 1% RM extract recorded at 1°C/min heating rate it was observed a slight splitting of the melting signal manifested as a shoulder. This can be explained by the disruption of the crystallinity of the polyethylene samples induced by the presence of 1% rosemary extract.

In Table 1 are shown the physical parameters and the crystallinity degree determined for LDPE and LDPE with 1% rosemary extract.

Table 1. Melting temperature (*T*m), melting heat (Δ*H*m), and crystallinity degree (*c*%) of untreated LDPE and LDPE incorporated with 1% rosemary extract obtained from µDSC measurements at different heating rates.

β (°C/min)	raw PELD		
	T_{min} / (°C) melting	**Δ*H* / (J/g) melting**	***c*** **%**
0.2	113.2	78.0	26.6
0.3	113.2	78.7	26.9
0.4	113.2	80.3	27.4
0.6	113.5	79.5	27.1
1.0	113.5	78.9	26.9
	PELD 1%RM		
	T_{min} / (°C) melting	**Δ*H* / (J/g) melting**	***c*** **%**
0.2	112.7	66.4	22.7
0.3	112.9	66.8	22.8
0.4	113.0	66.3	22.6
0.6	113.4	66.9	22.8
1.0	112.2; 114.5	65.2	22.3

A clear difference can be observed between the melting heats and crystallinity degree of polyethylene samples containing 1 % rosemary extract after 50 days of incubation with *Aspergillus Niger*. The results are shown in Figure 2 and Table 2.

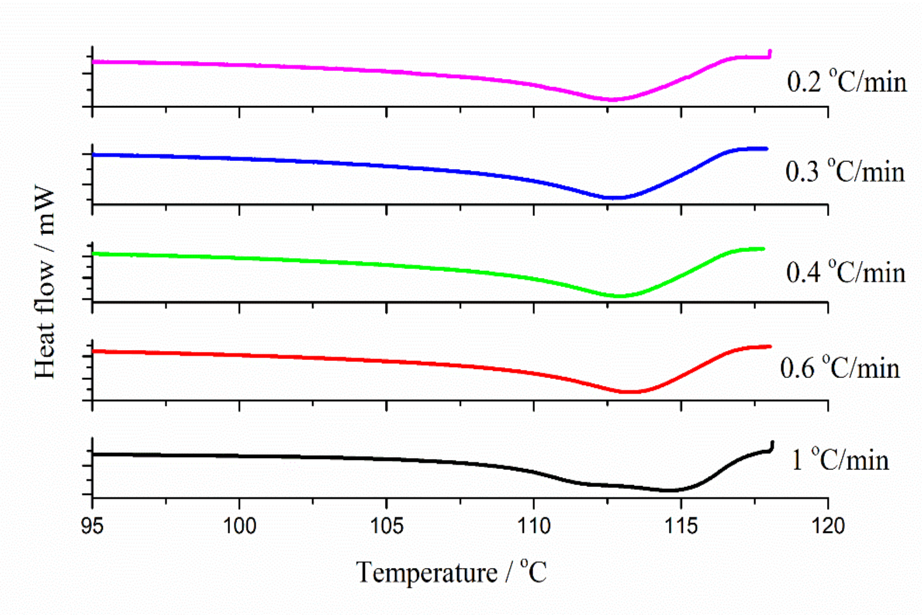

Figure 2. µDSC melting curves of LDPE with 1% rosemary extract after microbial attack with *Aspergillus Niger* at several heating rates, in nitrogen atmosphere.

From Figure 2 and Table 2 it was observed that the melting heats slightly increase after microbial attack, while the melting temperatures remain practically unchanged.

Table 2. Melting temperature (*T*m), melting heat (ΔH_m), and crystallinity degree (*c*%) of LDPE incorporated with 1% rosemary extract after *Aspergillus Niger* attack obtained from µDSC measurements at different heating rates.

β (°C/min)	PELD 1%RM after *Aspergillus Niger* attack		
	T_{min} / (°C) melting	ΔH / (J/g) melting	*c* %
0.2	112.6	67.2	22.9
0.3	112.7	67.9	23.2
0.4	112.9	67.7	23.1
0.6	113.4	67.1	22.9
1.0	114.7	65.6	22.4

From Table 2 one may also notice a slight increase in the crystallinity degree after microbial attack. This can be explained by microorganisms consumption of the amorphous part of LDPE with 1% RM extract.

Literature data reported that the polymers biodegradability started from their amorphous part [12]. The LDPE biodegradability can be correlated with the rosemary addition and degree of crystallinity of the obtained samples. Therefore, the incorporation of 1% rosemary extract into the LDPE matrix disrupts the structure regularity of the polymer chain. Moreover, the microbial degradation of LDPE occurs preferentially in the amorphous part of the polymer instead of its crystalline region [13]. An increase in the amorphous region and a low crystallinity of LDPE with 1% RM enhance the biodegradation of the polymer film. The present research demonstrates that rosemary extract acts as a disrupting agent by decreasing the LDPE crystallinity since the action of the *Aspergillus Niger* acts at the amorphous part of polymer.

4. Conclusions

LDPE and its composites with 1% rosemary extract have a high potential to be applied as packaging materials. The effect of rosemary extract content on modified polyethylene structure, before and after microbial attack, was evidenced. The experimental results and microcalorimetric analysis may serve for a better understanding of the relationship between structure and properties of biodegradable polymer blends. Eventually, this approach would be of significant interest and importance for modifying the properties and extend the practical application for biodegradable polymers from both academic and industrial viewpoints.

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