

Identification of several factors affecting biodegradation of aromatic-aliphatic copolyester

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Abstract — Aromatic-aliphatic polyesters aspire to be an eco-friendly replacement of conventional non-biodegradable polymers. Biodegradation of studied aromatic-aliphatic copolyester was estimated in soil and compost. The material was introduced into the tests in four forms differing above all by their specific surface. The copolyester in principle proved to be biodegradable under compost conditions. Biodegradation was also tested in five well selected and characterized agricultural soils. Here its biodegradability was not found to be significant. The specific surface of sample specimen was shown to be an important factor affecting the rate of biodegradation in compost, where biodegradation sample forms with higher specific surface was significantly accelerated over sample specimens with low specific surfaces.

Keywords — biodegradation, composting, copolyester, mulching film, soil.

I. INTRODUCTION

PLASTIC litter represents not only a serious environmental but also a social problem. Public is greatly alarmed at the omnipresence of plastic litter in the environment. The problem is particularly striking in less developed countries where functioning of waste management systems is insufficient. It should be pointed out that still the most recommended way of plastic waste treatment remains recycling but for many applications this approach tend to be economically not feasible due to the high cost of collection, separation and cleaning of the raw material. Plastic films are also still more extensively used in agriculture as mulching films. Here also the collection and especially cleaning is problematic.

In the past years growing interest is paid to the development of biodegradable polymers that could be able to replace conventional polyolefin films in many applications including mulching films and packaging applications [1,2]. The particularly perspective branch of such materials is represented by synthetic copolyesters with content of aromatic and aliphatic components [3,4]. Changing the component ratio one

is able to balance processing properties of the copolyester and its biodegradability [5,6,7]. In principle, aliphatic parts of the copolyester favor biodegradability of the polymer [8]. Several these materials were already commercialized and they are available on the market [9].

However biodegradation of such materials was not extensively enough studied especially regarding different conditions where and how the biodegradation should occur.

The present study deals with one particular example of the described materials. We wanted to show that its biodegradation can be greatly affected by the form of the sample specimen and can differ in various environments.

II. MATERIAL AND METHODS

A. Material

The polymer used throughout the study was aromatic aliphatic copolyester containing units of terephthalic acid, adipic acid and 1,4-butane-diol (molar ratio 22:28:50, respectively).

B. Polymer processing

Raw polymer in the form of pellets was processed to obtain different forms of the polymer with different specific surfaces.

Films. Films were prepared by compression molding at 140°C. According to the inserted steel frame films of 100 µm and 300 µm were prepared.

Powder. Chloroform solution of polymer (50 mg/ml) was poured into four volumes of ethanol and the mixture was vigorously stirred. Obtained precipitate was filtered out and dried on air. Resulting powder was characterized by microscopy (Fig. 1A, 1B). There were of irregular shape with diameters up to 500 µm. Electron microscopy with higher magnification revealed the important specific surface of the particles (Fig. 1B).

Thin coating on inert surface. Calculated volume (4 ml) of the chloroform solution of polymer (50 mg/ml) was applied on the surface of pre-weighed porous inert material (perlite, 7 g) and stirred. Then the solvent was stripped out with air leaving the polymer coating on the surface of perlite.

C. Biodegradation experiment

Three components were weighed into 500 ml biometric flasks: polymer samples (200 mg), mature compost or any of tested soils (5 g of dry weight) and perlite 7 g. Biometric flasks were equipped with septa on stoppers. Sample flasks

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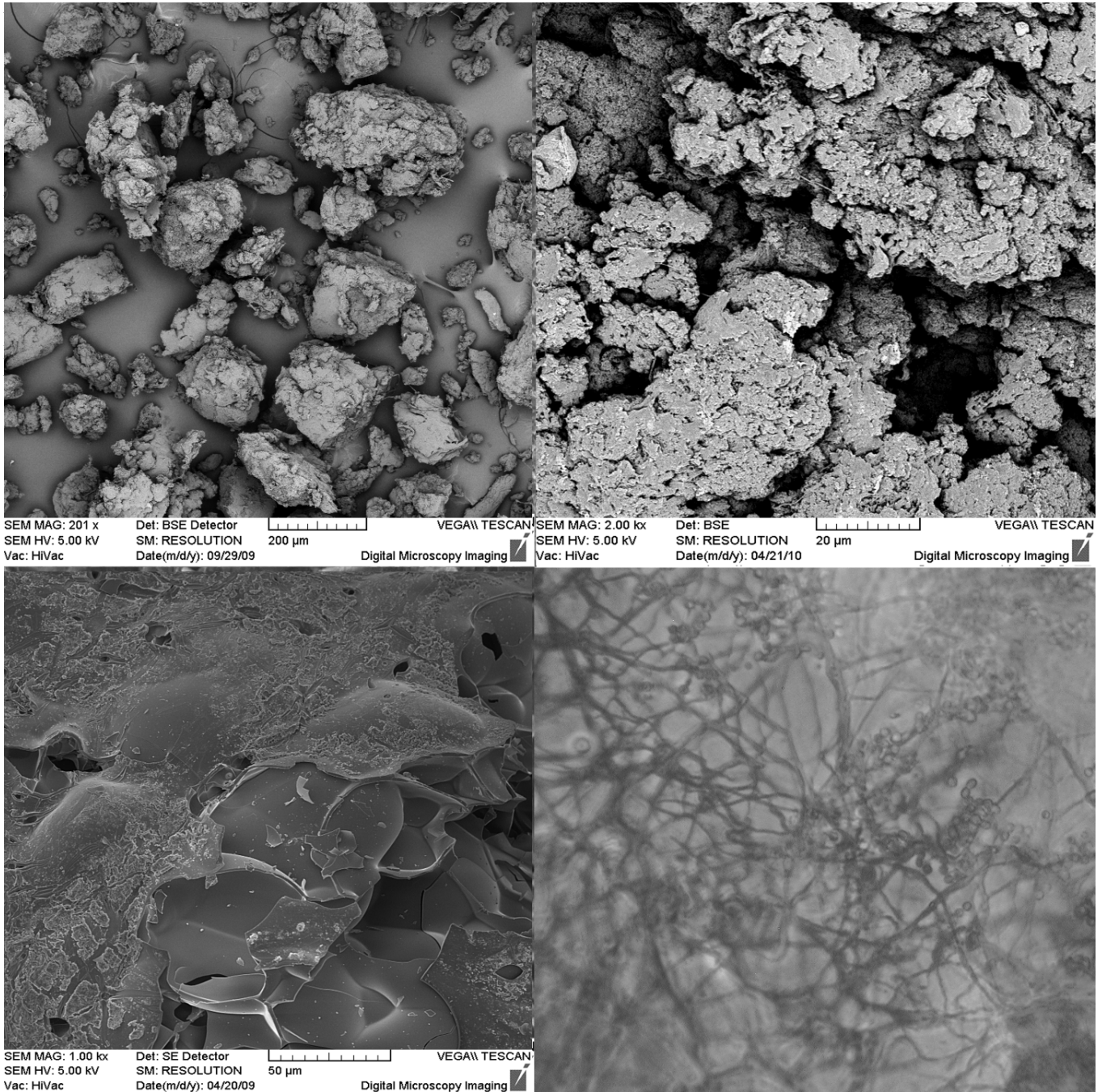


Fig. 1. A, electron microscopy of precipitated polymer powder (200 \times); B, electron microphotography of polymer powder at higher magnification (2000 \times) showing high specific surface of the powder particles; C, electron microphotography of polymer coating (upper left part of the microphotograph) on the surface of perlite (1000 \times); D, optical microscopy of bacterial filaments on the surface of 100 μm polymer film after incubation in compost (1000 \times), filaments were stained with carbolfuchsin and then observed under immersion oil, endospores typical for thermoactinomycetes are apparent as tiny nodules, the picture could not be made well focused everywhere because the film was not perfectly flat.

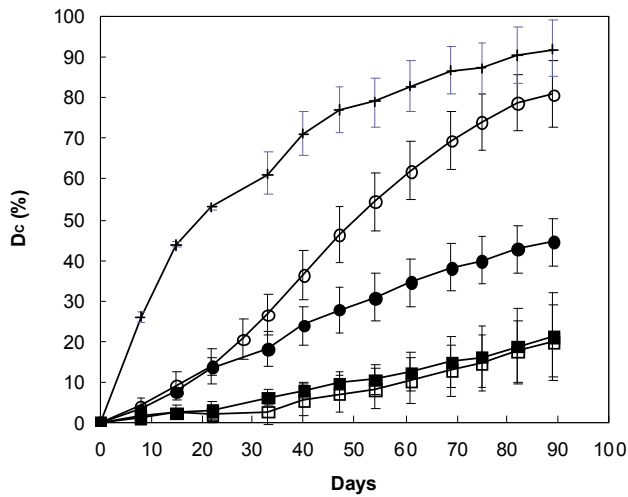


Fig. 2. Biodegradation of different forms of the polymer in compost experiment. □, thin film (100 μm); ■, thick film (300 μm); ○, powder; ●, thin coating; +, cellulose (reference compound). Error bars correspond to twice standard deviation ($n=3$).

D. Microscopy

For optical microscopy of the surface biofilm the polymer film fragment was fixed with 4% formaldehyde (overnight at 4°C) and then stained with carbolfuchsin. For scanning electron microscopy a polymer sample was coated with thin gold/palladium layer and observed in VEGA LMU (Tescan, CZ) instrument.

III. RESULTS

Investigated copolyester was designed to be a biodegradable material with potential applications in agriculture. Preliminary experiments showed (data not presented) that biodegradation of relatively thick compression (100 μm) molded polymer films appeared to be relatively slow. We decided to test whether this phenomenon was caused by low specific surface of the films. To answer the question we prepared two other forms of the polymer with higher specific surfaces, solvent precipitated powder of the polymer and deposition of the polymer on high specific surface inert material (perlite). Furthermore we intended to compare the polymer biodegradation under composting conditions and its biodegradation in a set of selected soils.

A. Biodegradation in compost

Results from compost experiment are well illustrated by Figure 2. Samples in forms of thin and thicker films behaved almost equally and end up with about 20% carbon mineralization after 90 days of incubation. Final values must be evaluated as relatively poor and hardly acceptable in an industrial composting plant.

However for the two forms of sample with higher specific surfaces the results are clearly more optimistic with about 45% carbon mineralization in the case of polymer coating on teh material with high specific surface (perlite). The fastest and most pronounced biodegradation was observed with the

powder of the polymer, where it reached more than 80% at the end of the observation period and was comparable with the biodegradability of microcrystalline cellulose powder used as a reference material.

B. Biodegradation in soil

Biodegradation of the described forms of polymer was also tested in soil environment. Five agricultural soils were used in the test and their classification types and basic structural and physical-chemical characteristic were determined (Table I). Basic microbiological characteristic were also obtained (Table II) to prove that all five soils were fertile and capable to support biodegradation.

However, the results of biodegradation experiments with all five soils were identical; in no one of the soils any significant biodegradation of any of the polymers forms was observed, levels of mineralization observed was not significantly different from zero.

IV. DISCUSSION

The polymer proved its good biodegradability under composting conditions. However, our experiments clearly showed that specific surface of polymer specimens affects greatly the rate of biodegradation. For most applications the polymer will be applied in the form of films with a relatively low specific surface and subsequently retarded biodegradation. It must be admitted that the films used throughout our experiments were thicker than films that would be prepared for real applications. We was not capable to prepare films thinner than 100 μm by compression molding, in real industrial

TABLE I
PHYSICAL-CHEMICAL PROPERTIES OF SOILS

Soil	Horizon	Soil type	Soil texture	pH H ₂ O	pH KCl	SOM %
S1	Plough layer	Eutric Cambisol	Loam	7.10	5.18	2.56
S2	Plough layer	Haplic Luvisol	Silty clay loam	6.44	6.33	1.67
S3	Plough layer	Haplic Chernozem	Silt loam	7.28	6.28	3.05
S4	Topsoil	Haplic Fluvisol	Silt loam	7.04	5.49	4.30
S5	Plough layer	Calcic Chernozem	Loam	8.06	7.52	2.07

pH H₂O = Soil pH in distilled water, pH KCl = Soil pH in M KCl, SOM = Soil organic matter [10].

production the film would be prepared by blowing process and

TABLE II
BASIC MICROBIOLOGICAL CHARACTERISTIC OF SOILS

Soil	Filamentous fungi	Aerobic chemoorganotrophs	Actinomycetes
S1	6.89×10^4	4.59×10^6	3.44×10^6
S2	3.78×10^3	5.26×10^6	2.92×10^6
S3	5.37×10^4	5.65×10^6	3.30×10^6
S4	2.25×10^5	9.81×10^6	6.18×10^6
S5	6.65×10^4	4.83×10^6	4.83×10^6

Numbers represents colony-forming units (CFU) per gram of soil dry weight.

would be thinner (about 20 μm).

On the contrary, the polymer revealed to be non biodegradable in soil environment at least under conditions and time scale defined in our experiments. This finding is not completely surprising, because biodegradation of similar materials in soil was not clearly reported in the literature yet. Also longer time studied polyester poly lactid acid (PLA) was shown to be virtually non-biodegradable in soil environment, while readily biodegradable under composting conditions [11,12, 13].

Reasons for such behavior of polyesters are not completely understood. It is known that extracellular lipases and/or peptidases play critical role during depolymerization process and make polymer fragments available for microorganisms. Thus higher ability of compost specific microbial communities to produce such enzymes could be an explanation of faster biodegradation of described polyester in compost environment. This explanation can be supported by the observation of biofilm of bacterial filaments bearing endospores (Fig. 1D) that could be tentatively identified as thermo-actinomycetes, which is the typical taxonomic group participating on the decay of organic matter in compost.

Not fully rejected there is still the hypothesis that polyesters can be hydrolyzed abiotically or enzymatically and the increased temperature in compost (about 60°C) kinetically accelerates the reaction.

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