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Degradation of PVC/rPLA Thick Films in Soil Burial Experiment

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Abstract. Some of the biodegradable polymers can be blended with a synthetic polymer to facilitate their biodegradation in the environment. The objective of the study was to investigate the biodegradation of thick films of poly(vinyl chloride)/recycled polylactide (PVC/rPLA). The experiments were carried out in the garden soil or in the mixture of garden soil and hydrocarbon-contaminated soil under laboratory conditions. Since it is widely accepted that the biosurfactants secreted by microorganisms enable biotransformation of various hydrophobic substances in the environment, it was assumed that the use of contaminated soil, rich in biosurfactant producing bacteria, may accelerate biodegradation of plastics. After the experimental period, the more noticeable weight loss of polymer films was observed after incubation in the garden soil. However, more pronounced changes in the film surface morphology and chemical structure as well as decrease of tensile strength were observed after incubation of films in the mixture of garden and contaminated soil. It turned out that as a result of competition between two distinct groups of microorganisms present in the mixture of garden and hydrocarbon-contaminated soils the number of microorganisms and their activity were lower than the activity of indigenous microflora of garden soil as well as the amount of secreted biosurfactants towards plastics.

1. Introduction

Poly(vinyl chloride) is one of the oldest known synthetic polymers. PVC in a pure form due to its low plasticity turned out to be technically useless and only its modification allowed to obtain materials for a wide variety of applications. Nowadays, PVC, because of some unique properties resulting from a wide spectrum of possible modifications, low price, chemical resistance and inflammability, is widely used in almost every sector of industry.

Polylactide is a well-known polymer of natural or synthetic origin. Many of its properties can be adjusted by the ratio of L-, D-isomers, although generally pure L-lactic acid is used for PLA production. It is believed that such polymer is prone to biodegradation after prior hydrolysis in humid environment under elevated temperature conditions (e.g. during composting). However, stream of post-consumer PLA packaging does not need to be recycled exclusively through composting. PLA after mechanical recycling can be reused e.g. as a filler increasing susceptibility of other polymers to environmental degradation.

The purpose of the study was the evaluation of the degree of degradation of PVC/rPLA compositions. Since packaging made of PVC is commonly used for storage of many substances such as oils, detergents etc., it was interesting to examine the influence of different substances on the properties of compositions. Such PVC/rPLA compositions cannot be composted which is why special attention was paid to biodegradation under mild temperature conditions in soil.

2. Materials and Methods

2.1. Materials

PVC compound was prepared by mixing PVC K70, dioctyl phthalate (Boryszew Erg, Poland) as a plasticizer and Ergoterm RC (Boryszew Erg, Poland) - composition based on calcium stearate as a stabilizing and lubricating agent in the weight ratio 100/55/3. PLA recyclate in the form of granules was obtained by extrusion of post-consumer PLA films. Both test materials were then homogenized and extruded. The extrusion process was carried out under the same conditions as for the PVC granules but at a reduced screw speed. Films about 1 mm thick were cut in the form of standard specimens (type 1A) according to ISO 527-1 standard, [1].

Parts of the test specimens were then subjected to three-month abiotic degradation by immersion in 96% ethanol, 10% sulphuric acid and mineral oil 15W-40. After exposure films were dried to a constant weight in a desiccator and weighed on an analytical balance (MS204S, Metler Toledo, USA). Before degradation in soils, each specimen was sterilized by immersion in isopropyl alcohol for 1 min followed by rinsing in distilled water for 3 min.

2.2. Soil burial experiment

Two types of soil were used in the experiment. Old garden soil was taken from the village Bojków while petroleum hydrocarbon (PH) polluted soil was taken from the vicinity of a 100-year-old oil refinery in Czechowice-Dziedzice. Other studies have shown that contaminated soil near refinery was rich in microorganisms able to excrete biosurfactants [2]. Both places are located in the Upper Silesia, Poland. Both soils were sieved through a sieve with a pore diameter of 2 mm. The first part of garden soil was put directly in the container. The second part of garden soil was mixed with the polluted soil in a volume ratio of 9:1 and then used in the experiment. Pristine and aged films prepared as described in 2.1 (Table 1) were then buried in the soils for five months. During the experimental period, soils were periodically watered and mechanically stirred in order to maintain suitable moisture and aeration. After the incubation period, the films were sterilized for 5 min in 1% mercury chloride and washed twice with distilled water.

2.3. Determination of selected soil properties

Moisture content was determined by a modified method suggested by [3]. Soil organic matter was calculated after combustion of dry-weight (dw) of soil samples in a muffle furnace at 500 °C for three days. Soil pH was determined according to [4].

In order to isolate biosurfactants, 20 g of soil was suspended in 40 ml of distilled water, sonicated at 50 $Jsec^{-1}$ for 2 min then shaken at 130 rpm for 24 hours. The soil suspension was centrifuged at 5000 rpm at 4 °C for 7 minutes. The supernatant was pressure-filtered through a 0.2 μm pore size filter and brought up to 100 ml with chloroform and methanol (2:1). The sealed flasks were shaken for the next 24 hours. Upper layer, after evaporation of solvents, was suspended in 30 ml of distilled water. Determination of the ability of biosurfactants to reduce the surface tension of water was analyzed by a method described by [5] using a tensiometer (Sigma 702, Attension, Finland).

To determine the microbial activity in soils, dehydrogenase assay based on the reduction of 2,3,5-triphenyl tetrazolium chloride (TTC) in soils was used [6].

Table 1. The composition of films, type of abiotic treatment and soils used in the study with abbreviations

Composition of films, % PVC/PLA (symbol)	Abiotic treatment (symbol)	Soil (symbol)
100/0 (PVC100)	control (C)	garden soil (S-)
65/35 (PVC65)	ethanol (E)	
50/50 (PVC50)	sulphuric acid (A)	mixture of garden and contaminated soil (S+)
0/100 (PLA)	mineral oil (O)	

2.4. Determination of the degree of polymer degradation
Weight loss of polymers was calculated according to [7]. For the purpose of scanning electron microscopy (SU 8010, HITACHI, Japan), random pieces of each sample were attached onto carbon-coated SEM stubs and sputter coated with gold for 40 sec. Tensile strength (R_m) and elongation at break (ε_r) of the samples were measured (TT-CM 80, Instron, USA) according to [1]. The FTIR/ATR spectra in the range of 4000-600 cm^{-1} were recorded using Nicolet iS10 (Thermo Fisher Scientific Inc., USA). All experiments described in the paper were conducted in five replicates.

3. Results and Discussion

It was found that the pH of garden soil and the mixture of soils were 5.95 and 5.36, respectively. Both soils were rich in organic matter, the content of which was about 12%. It has been reported that organic matter influences the activity of microorganisms as well as the enzyme production [8]. Some authors demonstrate correlation between organic matter and dehydrogenase activity in soil [9]. At the beginning of the experiment, dehydrogenase activity (DA) in both soils was similar and reached about 0.02 µgTPF g^{-1} dw h^{-1}. In comparison to other studies, enzyme activity was low [10]. The probable explanation is temperature of modified DA assay conducted, under the same conditions as biodegradation experiments, at 20 °C instead of standard assay at 37 °C. At the end of incubation period, a 10-fold increase in mean DA in garden soil and 5-fold increase in mean DA in mixed soils was observed. Previous experiments have shown that some polymer compositions may alter activity and growth of microorganisms in the environment (unpublished data).

The ability of biosurfactants isolated from garden soil to reduce surface tension was higher (19.4 mN ml m^{-1} g^{-1} dw) when compared to biosurfactants isolated from mixture of soils (13.24 mN mN ml m^{-1} g^{-1} dw). This phenomenon may be a result of competition between indigenous microflora of garden soil adapted to this environment and microflora of PH contaminated soil [11]. The most prominent weight loss of films about 25% was observed for rPLA while weight loss of films containing PVC did not exceed 5%. Additionally, higher weight loss of polymers was observed after incubation in native garden soil rich in biosurfactants (Fig. 1).

In the literature, there are some discrepancies concerning the influence of biosurfactants excreted by microorganisms on biodegradation of polymer. Aravinthan et al. [12] claims that polypropylene after contact with the biosurfactants becomes more hydrophilic and its biodegradation is more efficient because microorganisms are able to form a biofilm on the polymer surface. Furthermore, Sekhon, et al. [13] reported that the ability of microorganisms to secrete biosurfactants often correlates with increased esterase activity responsible for degradation of polyesters e.g. PLA. On the contrary, Fukuoka et al. [14] recently described that extend and rate of biodegradation of polymers may be fully controlled by pre-treatment with biosurfactants, which, when adsorbed onto the film surface, may even inhibit action of extracellular enzymes.

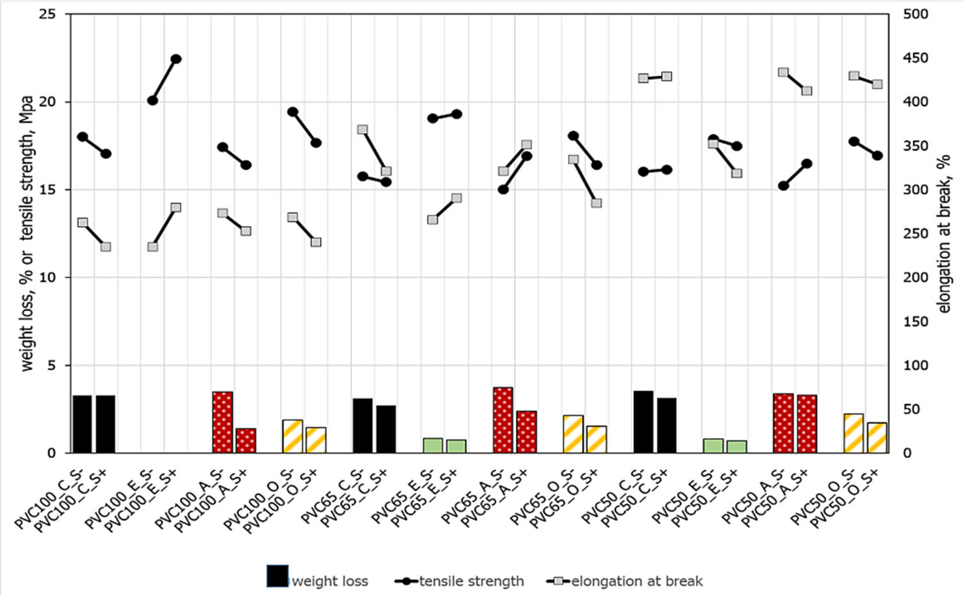

Figure 1. Weight loss and mechanical properties of films after abiotic treatment and burial in soils (abbreviations are explained in Table 1)

Moreover, the correlation between previous abiotic treatment and weight loss after incubation in soils was noted. Regardless of the amount of PVC in the compositions increasing weight loss of the films was observed in a series: alcohol < oil < acid < no aging. FTIR spectra revealed that after incubation in ethanol, plasticizer leached out of the films which became stiff (decrease in elongation at break) and resistant to biodegradation. During biodegradation of films after incubation in oil, microorganisms preferred residues of oil adsorbed to the film as the source of energy and carbon. Prior abiotic degradation in the acid had a negligible impact on the film thus did not alter the biodegradation of polymer.

In contrast to the SEM observations obtained by Aravinthan i in. [12], there was no visible growth of the microorganisms on the surface of polymers incubated in both soils (Fig. 2). It was concluded that degradation of films proceeded rather via indirect action of microorganisms through secreted biosurfactants as well as extracellular enzymes into the soil. Additionally, despite of lower weight loss, the surface of films incubated in mixed soil seemed to be more degraded than the surface of films incubated in garden soil. Similar results were described by De Campos et al. [15] after incubation of PVC/PVA blend in garden soil and garden soil mixed with the landfill leachate.

In this work, SEM observations are in agreement with the profile of tensile properties which showed that tensile strength and elongation at break of the films were generally lower after incubation in the mixture of soils. FTIR analysis revealed a substantial reduction in the intensity of C=O and C-H peaks that are characteristic for plasticizer in films incubated in both soils. However, sharp increase in the intensity of peaks in the range 1300-1000 cm^{-1} and 3500-3300 cm^{-1} and decrease in the peaks at 2900-2800 cm^{-1} confirmed SEM and tensile analyses.

4. Conclusion

The study highlights the effects of pre-treatments on biodegradation of PVC/rPLA compositions in different soils. Modification of PVC with rPLA did not increase the degree of decomposition of films when compared to pure PVC. Higher rates of weight loss were observed for untreated samples of compositions as well as for samples incubated in garden soil with high activity of microorganisms and rich in biosurfactants. Introduction of hydrocarbon-contaminated soil into garden soil has resulted in lowering the activity of microorganisms and the amount of biosurfactants being produced. However, more significant changes of other parameters such as mechanical properties, film texture and level of oxidation of films which were incubated in hydrocarbon-contaminated soil, have shown that biodegradation process proceeds with at least equal intensity but via different mechanism.

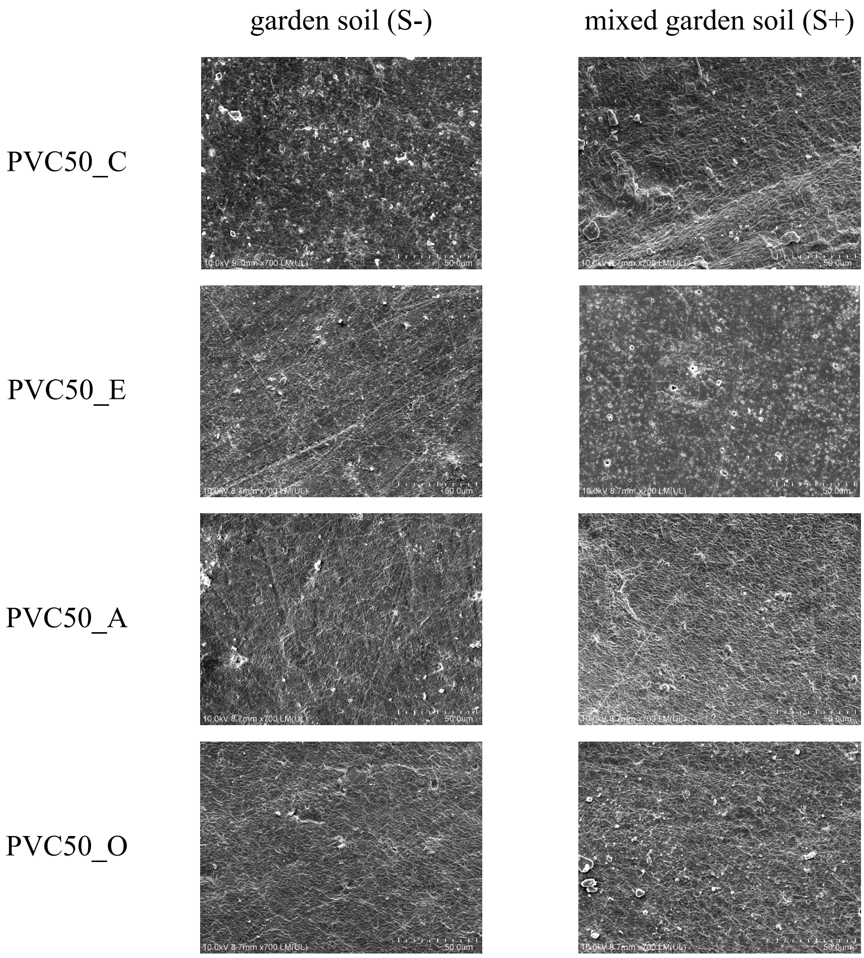

Figure 2. SEM photographs of the PVC50 films after abiotic treatment and incubation in the soils (abbreviations are explained in Table 1.)

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