Behavior of Composite Materials Under Microorganisms of Soil

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ABSTRACT: The article is devoted to the investigation of the dynamics of fungi and bacteria growth in different types of soil in dependence on the presence of composite materials based on polymers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3328–3332, 2007

Key words: composite materials; soil microorganisms; biodegradation; polymers

INTRODUCTION

Today polymers and composite materials on polymer base occupy a leading place in our everyday life. To preserve oil resources and to reduce wastes, a lot of biodegradable materials with the improved quality characteristics are being created.[1]

Biodegradable polymer materials can be divided into three groups: plastics based on natural biopolymers; chemically and microbiologically synthesized polymers and their mixes; and composite materials,[2] which contain biodegradable components, such as cellulose and its esters, starch, etc., that lead to biodamage of the whole composition. These materials are of special interest for practical utilization.[3,4]

Stability to microorganisms action of polymer materials depends on the used softeners, fillers, stabilizers, and different technological additives depends on their ability to be a source of carbon, nitrogen, and other biogenic elements.

Successful decision of the problem connected with biodecomposition of composite materials is closely related with the evolution of submission of the nature of the real processes of microbiological damages and presence of objective quantitative information about the regularity of their arising and proceeding.

The aim of this work was to investigate the behavior of composite materials on the base of series of large-capacity plastics under composting conditions for the creation of ecologically safe materials with different terms of utilization.

EXPERIMENTAL

The following materials were taken as polymer basis: acrylate-styrene carboxylated latex-Lentex A4; copolymer of ethylene and vinyl acetate (CEVA); copolyamide (Co-PA), received by polycondensation of adipinic and sebacic acids and hexamethylendiamine, trade mark-H-005 ($T_g = 115$–$120°C$, melting index, 15 g\10 min); thermoplastic polyurethane; polyvinyl alcohol (PVC). The criterion, governing the chose of the earlier-mentioned polymer materials, was the presence of functional groups in all these polymers. Another determining factor was the low temperature of their processing (130–150°C). This factor is rather important from the point of preservation of properties of fillers when getting samples.[5]

Organic and inorganic fillers were taken. Waste of grain thrashing were chosen as an organic filler, it has particles of 63–240 mkm in dimension, piled density (350 kg/m^3), and moisture (4%). Water soluble mineral complex fertilizer of type ''Rastvorin-A'' was used as an inorganic filler, which consists of the necessary microelements needed for growth and evolution of plants as well as the main trace elements, such as Mn, Cu, Zn, B, and Mo, in the form of their salts (Table I).

To compare the behavior of the prepared samples under composting conditions, composite materials were placed into soils of two kinds: sod-podzol soil (#1) and hothouse peat ground (#2). The samples were kept at 25°C during 5 months. The results were received with the help of the following methods:

- methods of analytical selection: microbiological investigations were directed on quantitative de-

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TABLE I
Qualitative Characteristics of ''Rastvorin A''

Nitrogen, in general (%)	10.0
Including $N—NH_2$	–
Including $N—NH_4$	5.0
Including $N—NO_3$	5.0
P_2O_5 (%)	5.0
K_2O (%)	20.0
MgO (%)	5.0
pH	3.0–4.5
Not soluble residue	<0.1

termination and definition of domestic forms of microorganisms.[6] Layers of soil were investigated, which directly surrounded the composted samples;

- chromatography-mass-spectrometry (Hewlett–Packard HP-6890 chromatograph);
- scanning electron microscopy (microscope JOEL-JSM-5300LV, Japan).

RESULTS AND DISCUSSION

It is a well-known fact that there is absolutely no stable action of microorganisms on polymers. Plastics are damaged by the following germs: fungi—*Aspergillus niger*, *Asp. versicolor, Asp. flavus, Asp. amstelodamii, Asp. ruber, Pen. purpurogenum, Pen. brevi-compactum, Pen. commune, Penicillium palitans, Cladosporium, Fusarium, Paccllomyces Penicillium sp., Aspergillus wamori, Aspergillus oryzae, Trichoderma sp., Chaetomim globosum, Trichoderma lignorum, Cephalosporum aeremonrum, Rhizopus nigricans, Alternaria*, *Candida*, *Lipolitica*, and *Sporatrichum sp.*—bacteriums: *Ptreptococcus rubrireticuli, Pseudomonas aeruginosa*, and *Streptococcus rubrireticull*.[7–15]

TABLE III
The Amount of Microorganisms Arousing in Soils While Composting Composite Materials Based on Different Polymers During 3.5 Months, KOE/g of Absolutely Dry Soil

		Chapek medium	
Type of soils	Polymer base	For fungi	For bacterium
No. 1	Polyurethane	2.05×10^6	1.15×10^7
	CEVA	2.79×10^6	2.30×10^7
	Co-PA	8.67×10^5	2.88×10^7
	Lentex A4	9.82×10^5	3.95×10^6
	PVC	2.39×10^6	6.13×10^6
No. 2	Polyurethane	3.76×10^6	1.38×10^6
	CEVA	4.87×10^6	1.09×10^6
	Co-PA	2.03×10^6	1.51×10^6
	Lentex A4	1.56×10^6	7.04×10^5
	PVC	5.17×10^6	1.24×10^6

It was revealed by us that the main part of the grown fungi on organic filler consists of *Penicillium*, also *Aspergillius* (*Asp. glaucus, Asp. restrictus, Asp. halophylicus,* and *Asp. candidis*) and *Thrihoderma* were present.

Fungi of *Penicillium u Aspergillius* genus are the most important types of soil microorganisms that influence mostly on preservation and quality of seeds and grains' waste. For this reason, they are called fungi of storage or molds of storage (while growing, they oppress a lot of other fungi, for example, *Cladopsorium* and *Trihcothecium*). Thus, composite materials, containing organic filler, have been already contaminated with fungi spores, arousing biodamage of polymer composite materials while being composted.

In Tables II–IV, the results on changing of microorganisms quantity in two soils (#1 and #2), while polymer composite samples composting during different testing times (from 2 to 5 months) are presented.

TABLE II
The Amount of Microorganisms Arousing in Soils While Composting Composite Materials Based on Different Polymers During 2 Months, KOE/g of Absolutely Dry Soil

		Chapek medium	
Type of soils	Polymer base	For fungi	For bacterium
No. 1	Polyurethane	1.12×10^6	1.88×10^7
	CEVA	5.00×10^6	1.55×10^7
	Co-PA	1.12×10^6	4.06×10^7
	Lentex A4	1.30×10^6	1.03×10^7
	PVC	1.85×10^6	2.15×10^7
No. 2	Polyurethane	2.65×10^6	6.50×10^4
	CEVA	8.10×10^6	8.4×10^4
	Co-PA	3.83×10^6	2.7×10^5
	Lentex A4	6.49×10^6	1.79×10^5
	PVC	2.47×10^6	2.20×10^5

TABLE IV
The Amount of Microorganisms Arousing in Soils While Composting Composite Materials Based on Different Polymers During 5 Months, KOE/g of Absolutely Dry Soil

		Chapek medium	
Type of soils	Polymer base	For fungi	For bacterium
No. 1	Polyurethane	5.56×10^5	5.11×10^8
	CEVA	4.30×10^5	4.92×10^8
	Co-PA	6.90×10^6	1.58×10^8
	Lentex A4	6.90×10^6	9.33×10^7
	PVC	6.90×10^5	3.76×10^7
No. 2	Polyurethane	2.56×10^5	2.37×10^6
	CEVA	6.21×10^6	5.89×10^6
	Co-PA	3.28×10^6	5.85×10^7
	Lentex A4	9.00×10^5	2.66×10^7
	PVC	2.97×10^6	4.25×10^7

TABLE V
The Quantity of Bacterium Existing in Soils While Composting Composite Materials Based on Different Polymers on Nitrite Agar During 2 Months, KOE/g of Absolutely Dry Soil

Type of soil	Polymer base	Mycobacterium	Arthrobacter	Nocardia	Micromonospora	Actinomyces	Total
No. 1	Polyurethane	8.14×10^8	5.53×10^8		5.60×10^7	7.50×10^7	1.11×10^9
	CEVA	6.27×10^9	1.24×10^8	2.00×10^7	2.00×10^7	1.04×10^8	6.55×10^9
	Co-PA	2.56×10^9	1.16×10^9	2.80×10^7	8.40×10^7	1.11×10^8	4.03×10^9
	Lentex A4	1.18×10^9	3.47×10^8	1.46×10^8	6.20×10^7	9.70×10^7	2.25×10^9
	PVC	1.99×10^9	5.14×10^8	7.30×10^7	2.40×10^7	2.82×10^8	2.57×10^9
No. 2	Polyurethane	2.92×10^8	1.05×10^8				5.26×10^8
	CEVA	4.48×10^8	1.81×10^8			1.70×10^7	8.93×10^8
	Co-PA	1.04×10^8	7.46×10^8		5.83×10^6	1.75×10^7	1.42×10^9
	Lentex A4	1.82×10^8	6.76×10^8			2.00×10^7	1.02×10^9
	PVC	0.98×10^8	2.50×10^8			1.60×10^7	4.97×10^8

As it is shown during the first two months, the fungi quantity on Chapek medium for fungi is the sample within the bounds of experiment and does not depend on polymer basis. Under aerobic conditions, fungi occupy the significant role in waste of grains decomposition,[16] and all that is confirmed during this experiment.

The quantity of bacterium and fungi in soil #1, with smaller amount of humus, is higher than in soil #2. Besides, microorganisms (*Penicillium*, *Aspergillius*, and *Thrihoderma*), being peculiarly present in organic filler, fungi of *Mycor, Rhizopus,* and *Fusarium* genus were revealed, which are characterized not only with low growth but also the ability to decompose aroma compounds.

Attention should be paid to the fact that a lot of actinomycetes have appeared after 5 months of composting in all soils. We have not mentioned about them during the earlier periods of composting. It is known that the formation of humus can take place while suppressing the microbiological processes.[17] Thus, in our case, at so active impact of fungi and bacterium mineralization of organic substances should be awaited.

At extension of composting time, the tendencies remain: in soil #1 with smaller amount of humus, the total quantity of microorganisms are more than in soil #2.

It should be mentioned that in spite of variety of fungi, *Mucor, Rhizopus* prevail in soil containing samples based on PBC, fungi of *Thrihoderma* genus prevail in soil with samples based on Lentex A4, and fungi of *Penicillium* genus prevail in soil containing samples based on Co-PA.

In Tables V–VII, the results on quantitative and genus changes in bacterium on nitrite agar at different testing times of composting of composite materials are presented.

As it is shown in Table V, the variety and quantity of bacterium in soil #1 is higher than in soil #2. *Nocardia* bacterium are absent in the soil enriched with humus. The quantity of bacterium of *Arthrobacter* genus is more in soils containing composite samples based on Co-PA, the quantity of bacterium of *Mycobacterium* genus is more in soils containing samples made of CEVA.

Mycobacterium and *Arthrobacter* fungi are characteristic for soils containing samples made of Co-PA, bacterium of *Mycobacterium* are characteristic for soils with samples made of PVC. Although *Micromonospora* bacterium are not typical for humus soils, but they well grow in soils with samples made of Co-PA and PVC. The quantity of *Actinomyces* bacterium during the whole period of supervision does not change practically.

TABLE VI
The Quantity of Bacterium Existing in Soils While Composting Composite Materials Based on Different Polymers on Nitrite Agar During 3.5 Months, KOE/g of Absolutely Dry Soil

Type of soil	Polymer base	Mycobacterium	Arthrobacter	Nocardia	Micromonospora	Actinomyces	Total
No. 1	Polyurethane	4.30×10^8	1.21×10^7		3.00×10^7	3.03×10^7	6.72×10^8
	CEVA	1.30×10^9	1.58×10^8	2.14×10^7	7.11×10^7	4.19×10^7	1.49×10^9
	Co-PA	5.64×10^8	1.65×10^8		5.14×10^7	2.92×10^7	7.77×10^8
	Lentex A4	1.03×10^8	7.52×10^7		1.54×10^7	7.53×10^6	2.06×10^8
	PVC	1.65×10^8	2.60×10^7		2.60×10^7	1.30×10^7	2.33×10^8
No. 2	Polyurethane	1.16×10^8	1.35×10^7	4.44×10^6		4.44×10^6	1.54×10^8
	CEVA	1.90×10^8	2.60×10^7			2.90×10^6	2.10×10^8
	Co-PA	3.87×10^7	2.29×10^7		3.28×10^6		6.62×10^7
	Lentex A4	4.85×10^7	1.58×10^7		5.37×10^6		8.02×10^7
	PVC	4.26×10^7			7.04×10^6		1.54×10^8

TABLE VII
The Quantity of Bacterium Existing in Soils While Composting Composite Materials Based on Different Polymers on Nitrite Agar During 5 Months, KOE/g of Absolutely Dry Soil

Type of soil	Polymer base	Mycobacterium	Arthrobacter	Nocardia	Micromonospora	Actinomyces	Total
No. 1	Polyurethane	6.86×10^7	4.47×10^7		1.37×10^7	3.43×10^6	1.30×10^8
	CEVA	6.96×10^7	2.78×10^7		3.48×10^6	6.96×10^6	1.04×10^8
	Co-PA	1.34×10^8	8.23×10^7	1.03×10^7	5.14×10^7	1.03×10^7	2.78×10^8
	Lentex A4	2.74×10^7	6.86×10^6				3.43×10^7
	PVC	1.13×10^8	2.74×10^7	6.85×10^6	1.71×10^7	1.71×10^7	1.75×10^8
No. 2	Polyurethane	8.67×10^8				1.03×10^7	8.72×10^8
	CEVA	1.39×10^9	9.28×10^7	2.32×10^7		2.32×10^7	1.53×10^9
	Co-PA	2.22×10^8	1.71×10^7		1.71×10^7		2.57×10^8
	Lentex A4	2.77×10^7	3.69×10^7	9.23×10^6		7.39×10^7	1.57×10^8
	PVC	7.11×10^7	1.78×10^7		8.89×10^7	3.56×10^7	2.31×10^8

In Table VIII, the results on quantity of arising CO_2 and CH_4 in different soils containing different composite samples are presented.

As it is shown from the Table VIII, we cannot say that the intensity of respiration depends on the type of soil. Excreta of CH_4 takes place in soil #1 depleted with humus after 3.5 months of composting. In soil #2, excreta of methane was noticed only in case with PVC samples. In bare testing, methane was not discovered.

The observed gas exchange is the sequence of breathing of waste of grain production, of breathing of microorganisms, and of chemical-oxidizing processes.

According to Ref. 18, breathing of waste of grain production is $\sim 1 \times 10^{-2}$ mg/g. Therefore, the decrease of the carbonic gas excreta can be explained both with depletion of organic filler as a result of microorganisms' action (Tables II–VII; Fig. 1) and with the fact that biomass of fungi is much more than biomass of bacterium.[19] So, the decrease of quantity of fungi (Tables II–IV) leads to the reduction of intensity of breathing.

During the experiment, changes in chemical composition of soil were revealed. Depending on the type of soil and samples in them, the educed organic substances are different.

Soil with smaller content of humus and with composite materials based on polyurethane holds stearic acid. The other soil was unadulterated, though polyurethane samples without any filler had numerous holes (Fig. 2) that are considered as the consequents of activity of microorganisms. Imid of dithiolcarbonic acid was revealed in the soil, with smaller content of humus and containing samples based on CEVA, after 3.5 months of storage while 1-nanodecene was present in the soil enriched with humus. ''Behavior'' of soils with samples based on Co-PA differs to each other: there was pyrimidinetetraamine in soil #1, and there was 1-isocyanododecane. Soils, containing samples based on Lentex A4 differ with the following: soil #1 keeps *N*,*N*-dimerhyldodecaneamid and 2-methyloximundecanon; soil #2 keeps 2-nonacosane. Allylmethylsulphide was found out in soil #1, containing samples on PVC, and imid of dithiolcarbonic acid was revealed in soil #2. Concentration of organic

TABLE VIII
The Quantity of CO_2 and CH_4 Excretion During Composting of Different Composite Samples in Soils

Type of soil	Polymer base	Testing time (month)					
		The quantity of CO_2, Mg/g of the sample			The quantity of CH_4, Mg/g of the sample		
		2	3.5	5×10^{-2}	2	3.5×10^{-6}	5
No. 1	Polyurethane	2.3	2.1	1.30	OTC	54.0	OTC
	CEVA	0.9	0.35	0.68	OTC	5.9	OTC
	Co-PA	2.7	0.30	10.45	OTC	17.3	OTC
	Lentex A4	1.2	0.24	0.32	OTC	6.2	OTC
	PVC	2.3	0.40	3.04	OTC	10.9	OTC
No. 2	Polyurethane	0.3	0.30	3.8	OTC	OTC	OTC
	CEVA	1.0	0.59	2.67	OTC	OTC	OTC
	Co-PA	3.7	0.27	10.67	OTC	OTC	OTC
	Lentex A4	0.7	0.13	3.2	OTC	OTC	OTC
	PVC	2.5	0.34	0.8	OTC	9.1	OTC

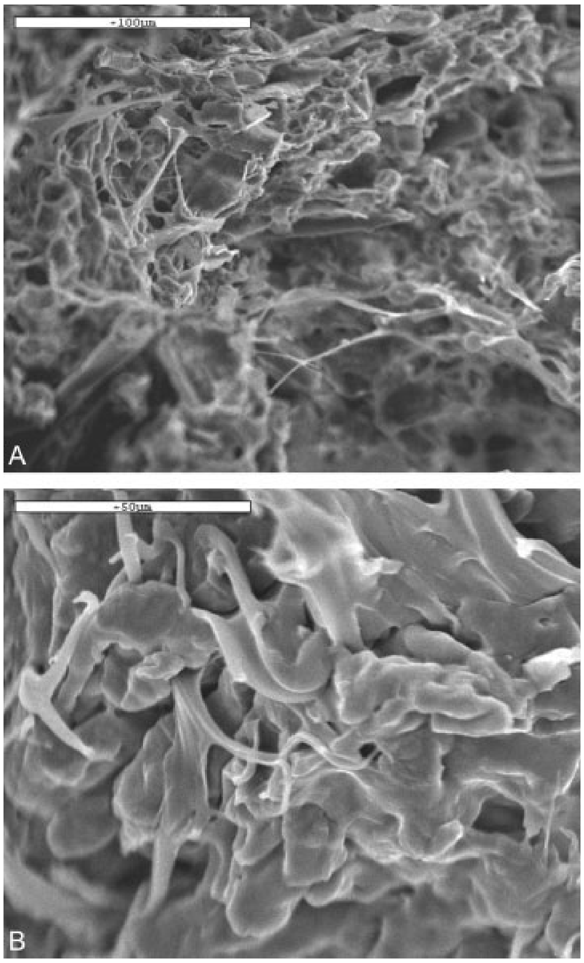

Figure 1 Electronic microscopical picture of ship surface of the filled with organic and inorganic fillers polymer matrix based on Lentex A4: (A) composted samples within 3.5 months; (B) initial samples.

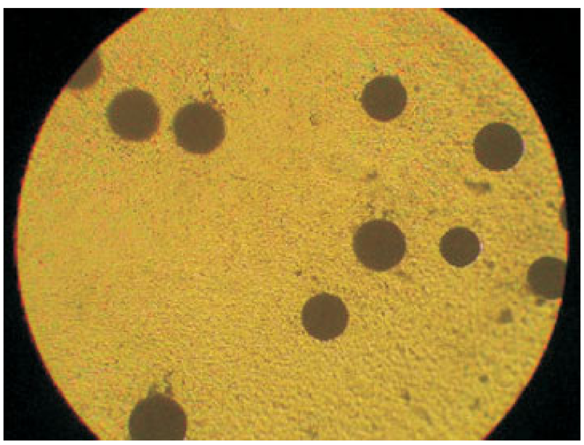

Figure 2 Photo of the ''holes'' on the surface of polyurethane samples without fillers being composted within 2 months. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

substances is 1×10^{-3}–5×10^{-4}% and it enlarges from 1.5 to 3 times with time duration. It has to be marked that the singled-out substances are not toxic to the environment.[20]

Thus, the change of dominating groups of microorganisms on the surface of composite materials in the process of their composting was revealed in the result of the carried out investigation. The quantity of fungi diminishes in 10 times and the quantity of bacteria enlarges as much times and dominates. The lowering of fungi quantity is connected with exhausting of easy to access organic and inorganic fillers, being part of composite materials. The growth of bacteria quantity is connected with the beginning of biological destruction and mineralization of polymer base.

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