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BRIEF COMMUNICATIONS

Microbial Degradation of Polyurethane

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Abstract—The process of decomposition of polyurethane samples in various soils has been studied.

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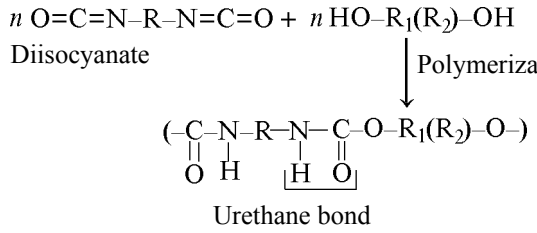
Ecological problems connected with burial of industrial wastes claim special attention to the processes of processing wastes and recycling of used plastic goods. Polyurethanes form an important and manifold class of man-made polymers used in a wide spectrum of goods in medicine, automobile production, and industry. The study and interpretation of the processes resulted from destructing polyurethanes are of practical interest.

Polyurethane is a common name of polymeric compounds obtained by polymerization of a diisocyanate and a diol having intramolecular urethane bonds:



Diisocyanates contain aromatic and aliphatic fragments. Toluylene and diphenylmethane diisocyanates are often used [1, 2].

Simple polyurethane is rarely acquisitive to microbial biodegradation. It was noted that some simple polyurethanes are destroyed by KN 11 strain *Staphylococcus epidermidis*, but the biodegradation passed very slowly as the mechanism of biological degradation includes an *exo*-type depolymerization [3].

The aim of this work was to study the mechanism of the biodeterioration of simple polyurethanes with the three-dimensional (sample I) and linear (sample II) structures by soil microorganisms.

The study of the decomposition of two polyurethane samples in soils within 20 months by IR spectroscopy has shown that the complete biodegradation of a polymeric compound does not occur irrespective of chemical compositions of soils. It is proved by the fact that the IR spectra of samples (after holding in soil) contain absorption bands corresponding to stretching vibrations of the associated imino group in the range of 3346–3340 cm^{-1} (s., br.) and of the carbonyl group (amide) in the range of 1734–730 cm^{-1} (s., sharp), ν_{C-H} in aryls in the range of 3010 cm^{-1} (s., sharp), ν_{C-H} in the range of 2924–2920 cm^{-1} (s., sharp), ν_{C-H} in the range of 2852–2850 cm^{-1} (s., sharp), $\nu_{C=C}$ in arenas in the range of 1597 cm^{-1} (s., sharp), to the bending vibrations δ_{NH} in the range of 1526–1524 cm^{-1} (s., sharp), etc.

The fact that the $-NH_{free}$ shoulder in the region of 3450 cm^{-1}, and also the absorption bands in the regions of 1665 ($\nu_{C=Oconj}$), 1122 (ν_{C-O-C} in ethers), and 885 cm^{-1} (ν_{C-C}), and one of the $C=C_{arom}$ stretching bands in the region of 1600 cm^{-1} have disappeared from the IR spectra points to a partial biodegradation of polyurethane sample II.

According to the IR spectroscopy data, the degradation of this polyurethane sample results from the hydrolysis of the ether bond:

$$\sim R^1O–R^2\sim + HOH \rightarrow \sim R^1–OH + \sim R^2–OH.$$

The electron microscopy of the initial polyurethane sample has shown that the both polymeric samples are characterized by the globular type of supermolecular structures (Figs. 1a and 1b). In the course of the polymer

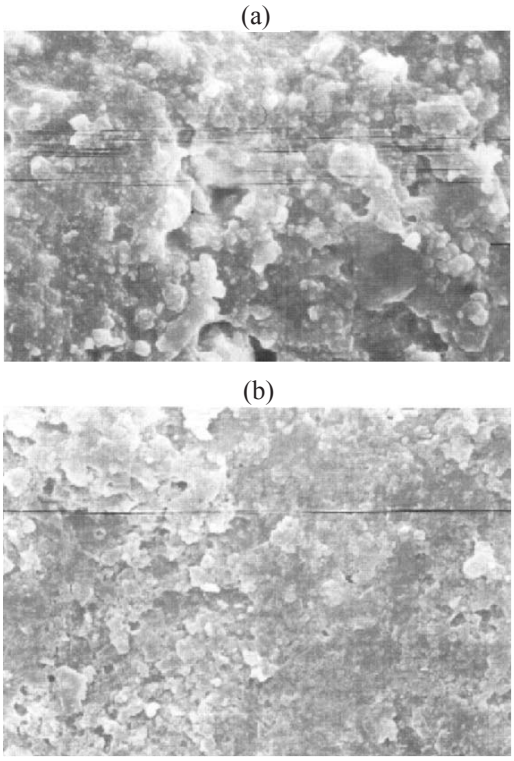


Fig. 1. Surface of reference samples (a) I and (b) II.

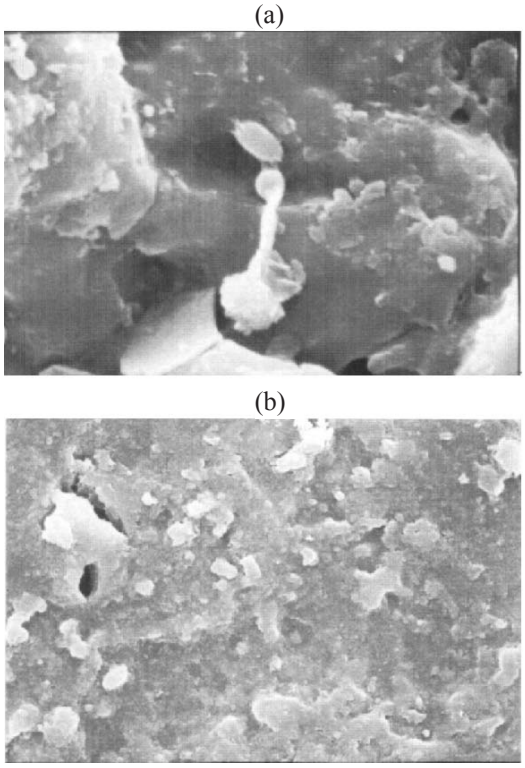


Fig. 2. Surface of reference samples (a) I and (b) II after incubation in a wood sod-podsolic soil.

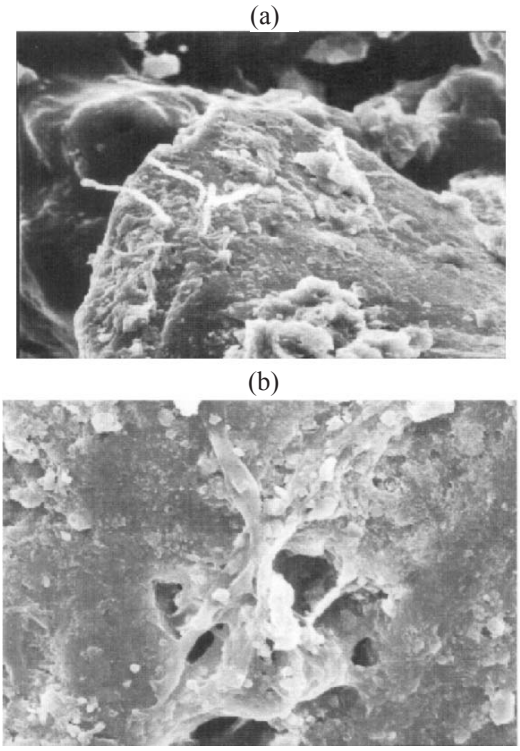


Fig. 3. Surface of reference samples (a) I and (b) II after incubation in a loam soil.

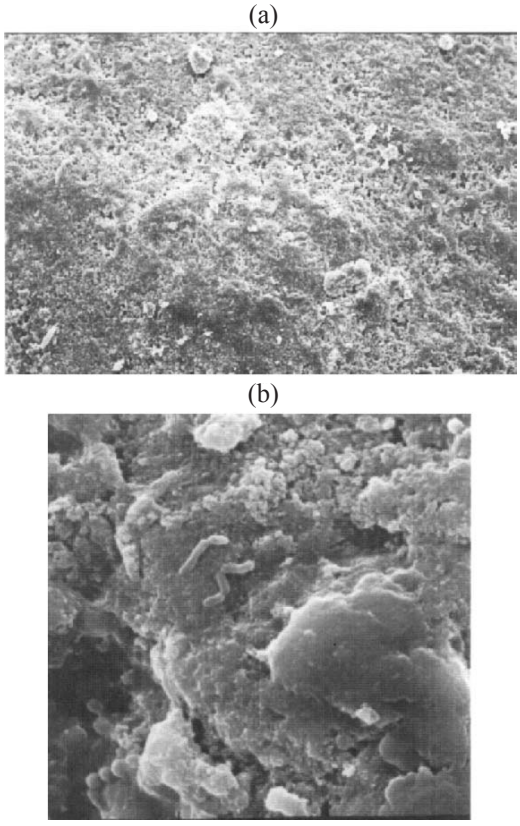


Fig. 4. Surface of reference samples (a) I and (b) II after incubation in a peaty-sod-podsolic soil.

Chemical composition of soils

Characteristic	Sample no.		
	1	2	3
pH aqueous	6.7	5.7	4.4
Hydr. acidity, mg-equiv/100 g	1.06	5.37	19.3
Sum of exchange bases, mg	32.5	20.41	2.86
Saturation degree of the bases, mg	96.8	79.2	12.9
Exchange acidity, mg	1.17	1.17	22.62
Al + H	0.78	1.56	42.12
Al	0	0	0.77
C, %	1.48	2.60	8.77
N, %	0.12	0.16	0.38
C/N	12.8	16.1	23.1
N, mg kg^{-1}	53.5	49.7	94.7
P_2O_5, mg kg^{-1}	26.7	24.9	47.4
K_2O, mg kg^{-1}	200.2	108.0	88.0

biological degradation the type of these structures was retained, but the size of globular structures varies. As a result of the incubation in soil sample no. 1 the polyurethane samples became covered by a heavy biofilm that points to the initial stage of a microbiologic damage, adhesions of microorganisms (Figs. 3a and 3b). As a result of the incubation the evolution of pseudo-mycelium of actinomyces and of mycelium of funguses was observed in soil sample no. 2 (Figs. 3a and 3b). These polymeric samples were subjected to the following microbialogic damage stage – the growth of microorganisms-biodestructors. The adhesion of cells of bacteria, rods, and coccuses was observed in the polymeric samples subjected to the incubation in soil sample no. 3 (Figs. 4a and 4b).

Thus, the electron-microscopy results have shown that the polyurethane three-dimensional sample is subjected to surface biological destruction, which does not change its chemical structure. The biological destruction of the polyurethane sample with a linear structure occurs both in a surface layer and in its volume and is accompanied by the disintegration of hydrolytically unstable bonds in the polymeric compound.

EXPERIMENTAL

The following samples were studied: (1) wood sod-podsolic soil; (2) dark grey silty loam; (3) peaty-sod-podsolic soil. Polyurethane granules were placed in soil for 20 months (T = 18–20°C). Chemical properties of the soils were determined by the standard technique [4]. The results of the fulfilled experiments are presented in the table.

The polymer surface was studied with a JMS-5400 (Jeol) scanning electron microscope, polymer samples were pasted on a two-sided carbon adhesive tape and covered by a gold layer sprayed in vacuum.

The IR spectra of samples of polyurethanes were recorded on a Shimadzu FTIR 8300 (Japan) IR Fourier spectrophotometer. The range of recording spectra was 4000-350 cm^{-1}, the error in the frequency under determination - 0.25 cm^{-1}. The samples under study were tabletted with potassium bromide (5 mg of a sample + 50 mg of KBr).

CONCLUSIONS

1. Complete polymer biodegradation does not occur irrespective of chemical composition of soils.

2. Polyurethane of a three-dimensional structure is subjected to a surface biodegradation, which does not change the polymer chemical structure.

3. Biological destruction of a polyurethane sample with a linear structure occurs both in a surface layer and in the volume and is accompanied by a decay of hydrolytically unstable bonds in the polymer.

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