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Surface Modification of Polypropylene Materials by the Cobalt Complex of 5,10,15,20-Tetrakis-(4-methylpyridyl)porphyrin Tetratosylate

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Abstract—The process of immobilization of cobalt(II) 5,10,15,20-tetrakis(4-methylpyridyl)porphyrin tetratosylate on chemically activated surface of polypropylene materials was studied using infrared spectroscopy of multiple frustrated total internal reflection, electron spectroscopy, and atomic force microscopy. The modified materials were shown to have a sorption activity with respect to nitrogen bases, the structural analogs of blood toxines.

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Among the urgent problems in the practical use of polymeric materials is the modification of properties of industrially produced polymers that allows extension of their area of use. In this context, of particular interest is the investigation of the possibility of directed regulation of the properties of the surface layer of the polymer products. Such modifications attract now much attention [1, 2].

Polypropylene materials are widely used in industry due to a number of valuable properties, but they also have shortcomings that limit their application. These deficiencies can be removed by various ways, including chemical surface modification [3-5]. However, polypropylene has practically no surface active functional groups allowing its direct chemical modification. Therefore, for preliminary surface activation of polypropylene the method of bromination is used followed by hydrolysis of the C–Hal bonds.

From a practical point of view, the high activity of porphyrins and their metal complexes is of great interest. In particular, for biological purposes porphyrin compounds soluble in water at the pH values near neutral are especially important. In this paper we suggest a method for surface modification of polypropylene materials by the water-soluble cobalt complex of 5,10,15,20-tetrakis(4-methylpyridyl)porphyrin tetratosylate.

Our studies showed that the chemical activation of polypropylene film surface leads to the appearance of the band in the region 500–700 cm^{-1} corresponding to the stretching vibrations of C-Br [7].

The subsequent hydrolysis of the carbon-halogen bonds with aqueous alkali (NaOH) leads to a significant increase in the concentration of oxygen-containing groups. After processing the brominated polypropylene in NaOH solution, the band at 600 cm^{-1} in the spectrum completely disappears and a band appears at 3400 cm^{-1} corresponding to the stretching vibrations of OH groups. The band at 2900 cm^{-1} probably characterizes the O–H stretching vibrations in H-bonded RC(O)OH compounds. The band at 1740 cm^{-1} corresponds to the vibrations of the carbonyl group [7–9].

To investigate the changes in the structure of the surface of activated polypropylene samples we used atomic force microscopy (AFM).

Figure 1 shows the AFM images in 3D mode of PP films with the original surface and chemically

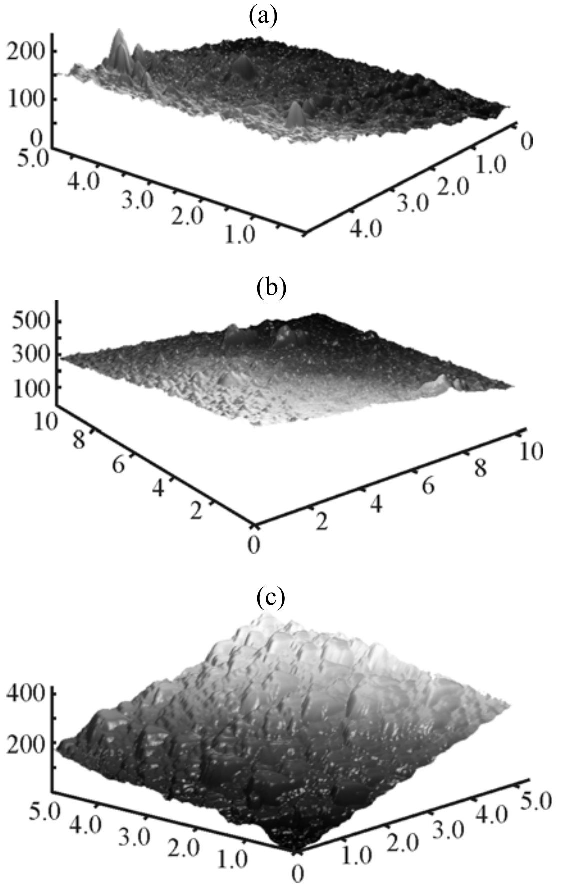

Fig. 1. AFM images of the surface of original and chemically activated polypropylene films in the 3D mode. (a) the original film, (b) film activated by the method *a*, and (c) film activated by the method *b*.

activated one. As seen, the activation leads to changes in the physical structure of the surface: its roughness is significantly reduced. Probably the oxidative degradation occurs in the surface areas of amorphous polymer, and peaks at images *b* and *c* correspond to the crystallites. This is due to breaking the relatively large spherulites into smaller ones.

Spectrophotometric studies using UV-VIS showed the presence of metalloporphyrins on the surface of modified samples.

The table lists the data on the immobilization of metalloporphyrin on a chemically activated surface of polypropylene by various ways. It is seen that the superficial concentration of CoTPyP is directly proportional to the immobilization temperature and duration. The optimum conditions of modifications for the studied materials were assumed 12 h duration at the temperature of 40°C.

Surface concentration of CoTPyP (N_S) was calculated using the known experimental values of the optical density ($A = \varepsilon cd$) of the layer of porphyrin complex. For CoTPyP $\varepsilon = 1.002\times10^5$ l mol^{-1} cm^{-1}, $A/\varepsilon = 2.92\times10^{-7}$ mol cm l^{-1} (Br_2 + NaOH, duration 12 h, 40°C). For the superficial density of the particles we obtain the following value: $N_S = (A/\varepsilon)\times N_A\times10^{-3} = 17.6\times10^{13}$ cm^{-2}. We calculated the effective area of the CoTPyP molecule by the method of molecular mechanics (force field MM+) using the program Hyper Chem (version 7): $S = 200$ Å^2. We find that the monolayer capacity $(1/S) = 5\times10^{13}$ cm^{-2}.

The experimental data also clearly show that the number of immobilized CoTPyP particles was a bit more on the samples activated by the method *b* (Fig. 2).

The dependence of the CoTPyP superficial concentration on the conditions of immobilization

Method of surface activation	Time, h	T, °C	Superficial concentration, $N_S\times10^{-13}$, particle/cm^2
Br_2 + NaOH	4	20	8.0
		40	11.0
		60	9.8
	8	20	11.5
		40	15.3
		60	13.4
	12	20	13.2
		40	17.6
		60	15.4
	16	20	14.5
		40	17.8
		60	15.3
Br_2	4	20	8.4
		40	10.8
		60	9.0
	8	20	12.1
		40	14.0
		60	10.2
	12	20	14.4
		40	16.6
		60	13.0
	16	20	13.6
		40	16.9
		60	13.2

The developed technique for surface modification of polypropylene film was transferred to the nonwoven geotextile polypropylene material to produce a sorbent for the purification of biological fluids from the nitrogen-containing metabolic products.

As a model nitrogen-containing substances we used an aqueous solution of creatinine with the concentration 8.1 mg l^{-1} (pH = 7.1), which was passed through a column filled with 4 g of the sorbent, the transmission rate 0.018 ml s^{-1}. The final concentration of creatinine determined spectrophotometrically (λ = 234 nm) was 5.3 mg l^{-1}.

The studies showed that the geotextile polypropylene material modified with CoTPyP can be recommended for the creation of materials with appropriate sorption activity with respect to nitrogen bases, the structural analogs of blood.

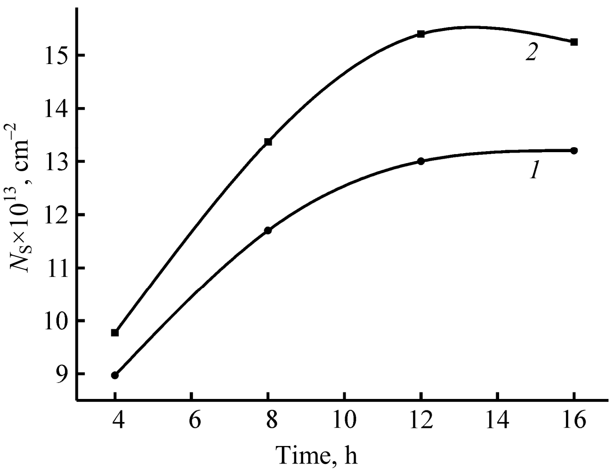

Fig. 2. The dependence of the superficial concentration of immobilized CoTPyP on the immobilization duration (T = 60°C): (*1*) film activated by the method *a* and (*2*) film activated by the method *b*.

EXPERIMENTAL

The measurements were carried out on a Fourier spectrophotometer Avatar 360 FT-IR ESP Nicolet using the prisms of zinc selenide crystal. The angle of incidence to the phases boundary was 45◦, the number of reflections was 12. The spectra were registered with signal accumulation from the result of 32 scans. The measurements were performed in the range of wave numbers 400–4000 cm^{-1}.

Surface structure of polypropylene films was investigated by atomic force microscopy (AFM) in the topography mode. The studies were performed on an atomic force microscope Solver P-47 Pro.

Electron absorption spectra were recorded using a scanning spectrophotometer Hitachi U-2000 with the accuracy of the wavelength ±0.1 nm, reproducibility of wavelength ±0.05 nm, photometric accuracy ±0.002 nm. The measurements were performed in the wavelength range 400–800 nm. To increase the level of the effective signal were used packages of 4 films.

We used a commercial film of isotactic biaxially-oriented polypropylene, produced in keeping with the specification TU RB 00204079.164-97 (molecular weight 400 000–700 000, thickness 20 μm), nonwoven geotextile polypropylene material (specific density 200 g m^{-2}), and cobalt 5,10,15,20-tetrakis(4-methylpyridyl)porphin tetratosylate (TPyPCo).

For the preparation of CoTPyP, to an aqueous solution of 5,10,15,20-tetrakis(4-methylpyridyl)porphyrin tetratosylate [9] was added freshly prepared insoluble metal hydroxide [solubility of $Co(OH)_2$ in water is 2×10^{-4}% by weight] at a ratio of 1:100, and the mixture was stirred with a magnetic stirrer for 8 h at 50°C. The formation of metalloporphyrin was monitored spectrophotometrically. For purification, the aqueous solution was filtered twice and then the complex was reprecipitated in a water-acetone mixture. The resulting precipitate was washed with acetone and dried at 75ºC, yield 96%. EAS of CoTPyP (water), λ_{max}, nm (log ε): 548 (4.05) 436 (5.00)

In this work we used the samples chemically activated by the methods *a* (bromination) and *b* (bromination followed by hydrolysis of the C-Hal) [4]. The composition of the superficial layers of the source and activated polypropylene was studied by the IR spectroscopy in the mode of repeatedly frustrated total internal reflection. Immobilization of CoTPyP on the surface of activated polypropylene was performed from a solution of CoTPyP in water (concentration of the solution of porphyrin 1.9×10^{-4} M) for 4–16 h at 20–60°C. The results of immobilization of porphyrins was monitored by electron absorption spectroscopy

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