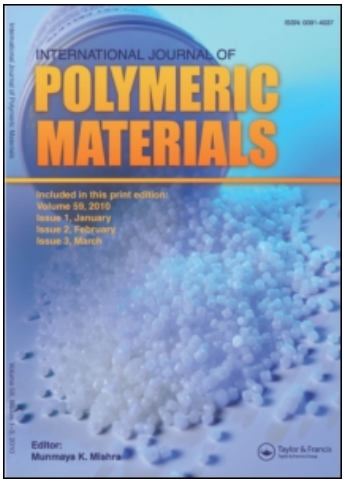

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Active Polymer Materials

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The technological importance of active polymer materials (APM) that exert physical, chemical or biochemical effects on contacting media or other materials is discussed. The experimental data show high APM efficiency in corrosion prevention, biopurifying, sealing, food packing and medicine. The mechanisms of APM effect on composition and properties of contacting objects are analyzed.

Keywords: Corrosion; biopurification; packaging; food; films; electrets.

1. INTRODUCTION

The need to solve global problems related to the limited raw material resources, the growing energy crisis and pollution of environment has caused over the last decades development of a multitude of commercial materials with additional functional properties. In addition to apart from their main function, which usually consists of supporting loads, such materials provide lubrication of friction units, prevent corrosion, seal machine part joints, etc. The best types of contemporary equipment are as a rule utilising multifunctional materials [1, 2]. A special place among them belongs to plastics capable of producing physical, chemical or biochemical effects on interacting objects. The growing production and application of synthetic polymers in place of traditional engineering materials, i.e. metals, ceramics, glass, wood is to a large extent related to the ability and convenience of using plastics as the technological base of APM.

According to the structure, their technological features and mechanisms of active effect on contacting materials and media, the APMs can be divided

into three main groups. The first one is represented by materials filled with magnetic [3, 4], electrically polarized [5–7], electrically or optically modified active compounds [2, 8, 9] or some other polymeric materials acting as the sources or transformers of physical fields. The second one includes polymer-based composites containing active low molecular mass or olygomeric solid, liquid or gaseous components, which attached various objects effect them chemically, electrochemically or biochemically [2, 10–17]. Some APM from the two groups are also produced by copolymerization of monomers [1, 18] carrying specific functional groups or by macromolecule functionalization. Plastics with immobilized microorganisms, enzymes or other active natural high molecular mass compounds represent a separate group [12, 19]. These APM require special production technologies.

In this article we discuss experimental data referring to the application efficiency of new APM developed by the authors. These APM include: a) polymer films for packing and corrosion proofing of metal items contain corrosion inhibitors (CI) and display electrochemical activity and b) polymer fibrous filtering materials (PFFM) carrying immobilized microbe cultures as well as packing films having food preservatives and natural antioxidant additives designed to protect meat products from microorganisms damage. In addition we analyze the effect of the plastics electret charge on spreading of oils relevant to a number of tribological and sealing problems, and estimate the therapeutic properties of APM filled with magnetic particles intended for medical application.

2. EXPERIMENTAL

2.1 Manufacturing Technology of APM

A. Films intended for corrosion prevention were produced using patented technology [20] from low density polyethylene (LDPE) on a sleeve film extruder equipped with a circular head. Saturated solutions of volatile corrosion inhibitors-tetrazole (Tet) or 5-phenyltetrazole (5-PhTet) in LDPE and di-(2-ethylhexyl)-sebacinate plasticizer (DHS, $\delta = 0.912$ g/cm^3) heated to 353 K were supplied into the space between the mandrel of extruder head and the sleeve. In order to increase the solubility of 5-PhTet up to 20% of benzene alcohol was added to DHS. The inhibitors were provided by the courtesy of Prof. V. A. Ostrovskii and Dr. V. S. Poplavskii of Sankt-Petersburg Technological Institute. The melting points of Tet (431 K) and

5-PhTet (485 K) corresponded to the published data. The extrusion rate was 0.1–0.3 m/s, the film sleeve diameter 1.0 m, the film thickness 100 ± 5 μm.

B. The PE films intended for packaging and microbe protection of meat products were produced similarly. In that case the film was modified by solutions of antioxidants and meat preservatives (ascorbic acid, coriander oil) in plasticizing fluid, i.e. medicinal vaseline oil. Nutrient type of mustard oil acting both as PE plasticizer and meat preservative was also used.

C. Tube-shaped filtering elements (inner diameter 40 ± 2 mm, wall thickness 5.0 ± 0.5 mm from non-woven PFFM (fiber diameter up to 50 μm, bulk density 0.22 g/cm^3) was produced by "melt-blown" technology [21]. Granules of polypropylene were melted in an extruder and the molten polymer extruded through a die. The fibers formed were dispersed by a stream of compressed air; the resulting gas-polymer mixture was directed onto the shape-forming support.

Active immobilization of biomass on the elements was conducted in a liquid medium containing a one day aged microbe culture. Complex strains were used, e.g. Bacillus cereus, Aeromonas sp. and Pseudomonas sp.. Immobilization process proceeded for 24–26 hours under conditions optimal for cultivation of the cultures; temperature = 300 K, pH = 6.5–7.5 and composition tailored for the medium.

D. Electret films 450–500 μm thick were produced from penton powder by compression moulding with subsequent formation of the electret state. Corona-induced electrets were produced by treating the films in corona discharge field. Thermally induced electrets were produced by treating the films in the constant electric field with intensity $E = 10^4 - 10^6$ V/m at 423 K for one hour. The field was removed after the samples were cooled to solidification.

E. Elastic magnetic materials (EMM) were produced in sheets by rolling at 400–425 K the mixtures of the polymer binder and barium ferrite plasticized by small quantities of dioctylpthalate. The mixtures composition included polyvinylchloride (5.0–10.0), nitrile rubber (2.5–7.0), barium ferrite (75–90), sulphur and technological additives. EMM technology is described in the patent [3].

EMM sheets were used to manufacture magnetotherapeutic carpets and magnetic applicators for footwear. The carpets were multipole magnetized in stripes or squares with chess-like sequence of the poles. The applicators in the shape of 20 to 50 mm diameter disks were magnetized to magnetic induction values $B = 20–30$ mT and were fixed in the footwear soles so as to contact the reflex zones of the foot.

2.2 Testing

A. Protection capability of anticorrosive films was evaluated using imitation technique. Flat steel or copper rectangular plates measuring $50 \times 50 \times 2$ mm were sealed into the film and kept for 72 hours at room temperature. Next they were placed into the testing chamber and subjected to cooling-heating cycles at relative humidity (RH) of the air $95 \pm 3\%$. The cycle included 8 h long exposure at 328 K followed by 16 h exposure at 298 K. After the test corrosion-induced damage of the samples was rated using the 10 grade scale (Tab. I). Corrosion sites in the form of individual points, blemishes, spots, threads, pits along with variations of colour or gloss were registered.

B. Full scale tests of the films containing food preservatives and antioxidants were conducted by packing meat into film napkins or thermally sealed packages. Packed pieces of the cooled meat (weighing 0.5 kg) were stored at $T = 278-280$ K. Several packages were opened after periods of time to control the organoleptic properties of meat, its microbe contamination and pH value the meat pieces surface [22, 23]. The guaranteed period of storage was set 24 hours less than the time needed for the first signs of waste to appear. The signs of meat waste included small changes of colour, odour, consistency and pH increase over 6.8.

The bactericide activity of the PE films containing food preservatives and antioxidants were studied using standard test cultures of the microbes Bacillus subtilis, Staphylococcus albus, Sarcina flavae, Trichoderma viride. The test microbe cultures were inoculated into the Petri dishes containing agar substrate and protein cultivating medium. The cups were kept in a thermostat at $T = 302 \pm 2$ K and RH 90% for 24 hours. The films bactericide activity was evaluated based on the width of the circular zones of the test-microbe growth suppresion formed around the samples.

To estimate the film effect on the microbe growth kinetics they were placed into the cultivating medium containing microbe culture suspensions with subsequent monitoring of the optical density of the suspension at the 750 nm wavelength using a photoelectric concentration colorimeter (Fig. 1).

TABLE I The Scale for Rating Corrosion Damage of Metal Samples

Surface of corrosion damage,	*up to*									*more than*
%	*0.05*	*0.1*	*0.3*	*0.5*	*1*	*3*	*5*	*10*	*30*	*30*
Corrosion severity	1	2	3	4	5	6	7	8	9	10

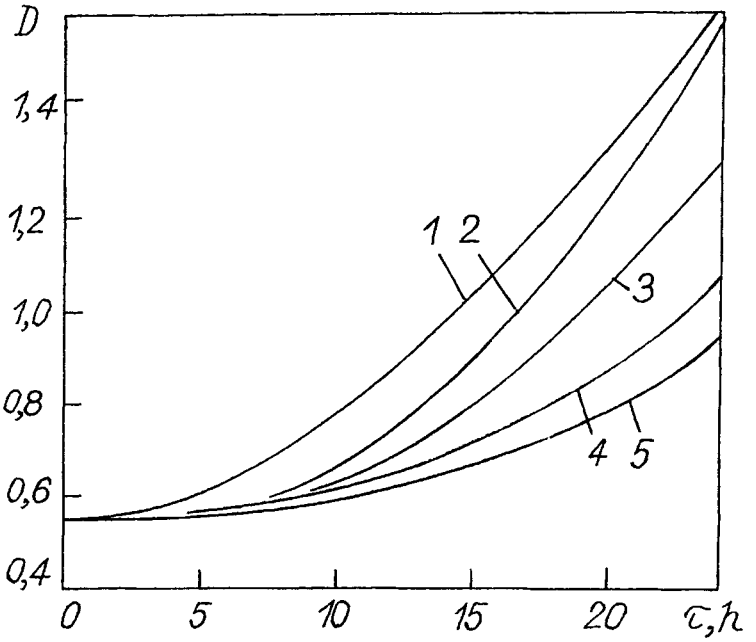

FIGURE 1 Optical density of the test microbe Sarcina flavae suspensions in cultivation medium versus time: 1-control, 2–5 in contact with films from initial PE (2), PE modified by ascorbic acid (3), mustard (4) and coriander (5) oils.

Physiological harmlessness of the films was tested at the Belarus Scientific Research Institute of Sanitation and Hygiene. Chemical composition of the model media (distilled water, 0.3–3.0% solutions of citric acid) after 240 h contact with the active films was anlayzed using gas chromotographic technique. Migration levels of the toxic substances from the films were compared with the limiting permitted values equal (in mg/l) 0.1 for formaldehyde, 0.2 for methanol and 0.05 for phenol. Besides, organoleptic qualities of the extracts were assessed.

C. Specific sorption of biomass on non-woven PFFM support was determined gravimetrically as the mass increment following immobilization procedure. The by-products present in the immobilization medium were thoroughly washed off the samples sequentially by hydrochloric acid water solution, chloroform and distilled water.

The performance of the biosubstrates based on PFFM was studied at the Russia State Institute of Applied Microbiology (Obolensk). The capacity of the laboratory bioreactor was 5.3×10^{-3} m^3, the volume of the filtering packing 4.6×10^{-3} m^3, the thickness of the filtering layer 1.75 m. The filters

were used to purify heavily polluted toxic sewage of a chemical plant. It contained (mg/l) isopropanol-770, ethylhexanol-2538, chloroethylhexyl-1840, acetone-900, methyl isobutyl ketone-200, esters-200, diacetone alcohol-30, sodium chloride-1200, mesityl oxide-100, toluene-50. Chemical intake of oxygen (CIO) was 14.1 g/l. The sewage discharge was varied between 0.1 and 0.6 m^3 per 1 m^3 of the packing over 24 hours. The air flow rate was maintained constant at $1m^3/1m^3$ of sewage per hour. Efficiency of purification was estimated based on the decrease of sewage total contamination given by CIO value following purification relative to the initial value. Purification efficiency for individual contaminants was determined using gas chromatography.

D. Contour variation of diethylene glycol or glycerine drops spreading over the electret films surface and equilibrium wetting angles were registered using an optical microscope equipped with goniometric scale eyepiece at 200 magnification. A drop of liquid having the volume of 5×10^{-10} m^3 was applied onto the film surface using a microsyringe. The initial spreading rate was calculated from the dependence of the drop base radius versus time. The surface charge density of electret films was measured using the compensation contact-free method [24].

E. Sanitary-chemical investigation of EMM was conducted at the Russia Scientific Research Institute of Medical Technology including evaluation of the concentration of low molecular mass substances migrating from EMM, allergic effect of extracts after multiple application on the skin of white rats and the contact effect of materials on the state of skin of human feet.

The magnetic therapeutic activity of the carpets and the footwear with EMM applicators was studied at the laboratory of clinical bioenergetics of the Central Scientific Research Institute of Traumatology and Orthopedia named after N. N. Priorov (Moscow) and at the departments of functional diagnostics and operative surgery of Vitebsk Medical Institute. The EMMs were used for treating patients aged 20–45 years suffering from hypertonia, obliterating vascular diseases of legs, arthritis, heel calcar, platypodia and bursitis of metatarsal-phalanx joint. The treatment course continued 10–15 days (30–60 min daily contact with EMM). It included regular measurements of blood pressure, central and peripheral hemodynamics, skin thermometry and other clinical and biochemical analysis.

3. RESULTS AND DISCUSSION

A. Earlier we applied the potentiodynamic method to study the effect of 5-R-tetrazole (R=H, CH_2, NH_2 etc.) additives, as well as potassium and

sodium salts of 5-phenyltetrazole on kinetics of steel and copper electrochemical reactions in 0.05 M water solutions of sodium sulfate imitating the aggressive medium in conditions of atmospheric corrosion [25]. The compounds were established to be universal corrosion inhibitors (CI) for ferrous and non-ferrous metals and excelled in some cases benzotriazole. Besides, the high thermal stability, volatility (the pressure of the saturated vapour is 10^{-3}–10^{-2} Pa at 293 K) and bactericide properties of the tetrazoles determine their selection as electrochemically active components of polymer films. The latter are used to pack and preserve metal items from atmospheric and microbiological corrosion.

Electrochemically active films produced according to the technology described above [20] have a modified layer 30–40 μm thick from the inner side of the sleeve. It represents a porous polymer matrix with the pores filled with CI solution in a plasticizing fluid. The matrix experiences relaxation processes accompanied by syneresis. When the film is used for packaging metal items, the CI contained in the modified layer is released into the space inside the package, through evaporation and together with the plasticiser through syneresis. So the active component is transferred onto the surface of protected objects.

The steel and copper specimens sealed in films modified with Tet and 5-PhTet inhibitors respectively had no traces of corrosion (corrosion 0 or 1 on tarnishing) after 22 test cycles. The same specimens showed corrosion level of 6–8 severity when sealed into regular PE film.

The composition and the strucutre of the steel specimen surface layers before and after their exposure in film packages modified with the tetrazole were studied by the X-ray photoelectron and multiple internal reflection IR spectroscopies, atomic force and scanning electron microscopies. It was established that the surface of exposed specimens is modified consisting of an adsorbed 6.8 nm thick film. This surface layer is composed of clusters of $[Fe(CN_4H)_2\ (H_2O)_2]$ complex compounds having stereoregular chain structure stable in water and many organic solvents.

Evidently the mechanism of protection of steel items by polymer films containing tetrazole additives includes release of CI from the film into the sealed space, its diffusion to the metal surface and dissolution in corrosion-active condensed water medium. The adsorbed layer based on coordination compounds "Fe-Tet" emerging at the metal-electrolyte interface bars the transport of reactants to the zone of electrochemical reaction and the release of products from this zone. As a result of this process the corrosion is either prevented or its rate reduced.

Since 5-R-tetrazoles tend to produce complexes with copper salts [26] it may be assumed that the mechanism of copper protection by films containing 5-PhTet is similar to the one suggested for the system tetrazole-steel.

B. Packaging films modified with food preservatives and antioxidants are similar to the anti-corrosive materials in structure and mechanism of transporting the active component to the protected object.

Full scale tests have shown that guaranteed storage time for cooled meat products packaged in microbiocide films equals 6–8 days which is two to three times longer compared to the storage time in inert LDPE packaging film. The meat packaged in the film modified with ascorbic acid may be stored at ambient temperature for 36 h preserving its taste and flavour.

According to the results of microbiological testing the films modified by mustard and especially coriander oils show pronounced antimicrobe activity (Tab. II), ability to inhibit the growth of bacteria and mold fungus (Fig. 1). This is less characteristic of films containing ascorbic acid. The favorable effect of packaging on meat in this case is caused mainly by the antioxidative properties of the active additive. Thus, it was established that the films modified by the solution of ascorbic acid in vaseline oil display reduced permeation to oxygen compared with original LDPE films despite the presence of a porous layer in their structure.

The sanitary-chemical tests have revealed that aqueous and water-acidic extracts from microbiocide films have satisfactory organoleptic properties. Transport of the toxic compounds from the film samples into the model environment is either absent (methanol, phenol) or it remains within permissible limits (formaldehyde). The use of the films as packaging materials contacting raw meat and meat products has been permitted in Belarus by the Health ministry.

TABLE II Indicators of Bactericide Activity of Packing Films Containing Food Preservatives and Antioxidants

Sample	*Width of zone of test-microbes suppresion*			
description	*Staphylococcus albus*	*Bacillus subtilis*	*Sarcina flavae*	*Trichoderma viride*
LDPE film	0	0	0	0
LDPE films modified with				
coriander oil	50–60	2–3	3–4	2–3
mustard oil	40–50	1	1–2	1–2
ascorbic acid	1–2	0	1–2	0

An advantage of bactericidal films is their ease of recycling compared to multilayered packaging materials used in food industry.

C. The sorptional capacity of non-woven PFFM elements based on polypropylene is higher in respect to the studied microorganism strains compared to the regular carriers of the biomass in filters. It reaches respectively (mg/l) 7.6 for PFFM, 4.4 for claydite, 1.6 and 0.6 for large pores and fine pores ceramics, 2.6 for granular polyurethane foam.

The data concerning efficiency of sewage biopurification of a chemical plant using pilot biofilters equipped with PFFM packing are presented in Table III. Biopurification proceeded with high efficiency. According to the results of gas chromatographic analysis it ranged between 34 to 100% for various substances. After 2 months service the PFFM filters showed no signs of degradation. In terms of capacity to ensure efficient biopurification and technological properties PFFM are as good as the carriers listed above. The advantages of PFFM include low density and hydrodynamic resistance, short start-up period, low cost of the elements if polymer waste is used for their manufacture.

D. Table IV presents the data on spreading of a model viscous fluid (diethylene glycol, DEG) on the positively charged polymer electret films. The increased density of the electret surface charge (δ) reduces the initial rate of spreading provided the other conditions remain unchanged. In addition, the equilibrium wetting angles θ increase. When δ of a thermoelectret increases from 1 to 6×10^{-6} C/m^2 cos θ of glycerine diminishes from 0.45 to 0.25. Electrical polarization is likely to change the supermolecular structure of the film surface layer and the physico-chemical characteristics of DEG. As a result the wetting and spreading are modified presumably through emergence of additional energy barrier which brings in a negative contribution into the driving force of spreading.

TABLE III Indicators of Purification Efficiency of Pilot Bio filters with PFFM Packing for Chemical Plant Sewage (CIO 14.1 g/l)

Sewage discharge m^3/m^3 of packing per 24 hours	*CIO, g/l after purification*	*Purification efficiency, %*
0.10	1.2	91.5 (young biofilm)
0.16	0.4	97.2
0.25	1.2	91.5
0.48	2.0	85.8
0.60	2.5	82.1

TABLE IV Initial Spreading Velocites (v) of DEG on Surface of Penton Films in Relation to Film Surface Charge Density (δ)

Sample type	$\delta, C/m^2$	$v, 10^{-4}$ *mm/s*
Control	0	2.8
Thermal electret	$4.96\ 10^{-6}$	1.4
	$2.78\ 10^{-3}$	0.6
Corona electret	0.36	0.4

Experimental data presented indicate that APM can be recommended for application in sealing systems. The electret field controls the kinetics of the fluid capillary penetration along the clearances of the contact seals.

E. The results of the EMM sanitary-hygienic checks are positive. The volume of sodium thiosulphate to titrate the EMM extracts equals 0.3 ml (the standard allows 1.0 ml) and the pH shift 0.5. Irritating or allergic action of the extracts on white rats skin was not revealed.

The therapeutic effect of the EMM-based applicators included a decrease of the arterial pressure by 20–40 mm Hg for patients with hypertonia. The patients suffering from vascular and other diseases of the legs showed an increase of the skin temperature of 0.2–0.6 K, improved status and decreased pain syndrom after 3–4 procedures. In cases of metatarsal bone fracture the resolution of edema and formation of bone callosity proceeded faster.

Ministry of Health of the Russian Federation permitted the footwear with magnetic applicators to be used as magnetotherapeutic aid.

4. CONCLUSION

The presented data show that APM represent a rapidly developing class of materials having potential for application in various fields of technology. Although the traditional materials are still to a large degree retaining their markets, the emphasis in material science is now on development of active multifunctional materials and search for their most efficient application. In this context it is important to understand the mechanisms ensuring APM additional functional properties and to develop control of the factors responsible for their physical, chemical or biochemical activity.

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