INSECTICIDAL FILMS FOR NON-FOOD PRODUCTS PACKAGING

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Обсуждаются результаты исследований по разработке технологии получения инсектицидных биоразлагаемых полимерных пленок на основе пластифицированных композиций «крахмал-полиэтилен». Рецептурные, температурные и реологические параметры процесса оптимизированы по комплексу наиболее важных эксплуатационных характеристик пленок (прочность, биоразлагаемость, инсектицидность и др.).

Results are discussed of investigation aiming to production technique development of insecticidal biodegradable polymer films based on plasticized starch-polyethylene compositions. Formulation, temperature and rheological parameters of the process have been optimized by a complex of most significant film performances (strength, biodegradability, insecticidity, etc.).

Ключевые слова: *инсектицидная пленка; биоразлагаемый полимер; непродовольственные товары.*

Keywords: *insecticidal film; biodegradable polymer; non-food products.*

The tendency to straining problems in global raw materials, power and ecology has lead to a new approach to the development of polymeric packaging materials [1; 3; 5; 11; 13]. The latters are to carry out not only barrier and mechanical functions but are to exert an active influence on the neighbouring media and objects. Used in packing industry multifunctional polymeric materials correspond to these criteria. Considered in this paper insecticidal biodegradable films (IBF) belonging to above class of materials are intended for packing keratin-containing items of light industry. They are woolen fabrics, clothes, footwear, semi-finished fur items, furniture, etc.

The aim of the present work was to produce a high-quality packing IBF with a complex of required performances, to optimize film production technique by are technical and economic criteria as well as to elaborate control methods over their destruction for fast and safe recovery of used packing.

Polyethylene (PE) of high and low density was used as a base polymer. Corn starch (St) plasticized by glycerine carried the role of PE filler. St is a widespread product of vegetable processing and is an alternative to traditional mineral fillers. Its usage solves not only the problem of resource saving but furnishes support to agriculture due to expansion of the agricultural market.

St is not a film-forming substance. At synthetic polymer modification by St it is necessary to use plasticizers raising compatibility of components and improving physico-mechanical characteristics of filled materials. Plasticizers (dyethylene glicol, dimethyl- and dioctylphtalate, vaseline oil and their mixtures with glycerine) have been investigated as to compatibility criterion with PE, St and insecticidal additive. The selection of insecticides from the class of pyrethroids (permethrin, cypermethrin, deltamethrin, etc.) is conditioned by their non-toxicity towards warm-blooded [2; 10], high efficiency of functional (insecticide) action and sufficient thermal resistance at processing together with polymer melts. The study results of above mentioned plasticizing liquids compatibility with permethrin are given in table 1.

Table 1

Permethrin compatibility with plasticizers

Plasticizer	Temperature, K and plasticizer : permethrin proportion (mass)									
	297 K					338 K				
	1:1	1:2	1:3	1:4	1:5	1:1	1:2	1:3	1:4	1:5
1. Vaseline oil	–	–	–	–	–	+	+	+	+	+
2. Glycerine	–	–	–	–	–	–	–	–	–	–
3. Dioctylphtalate	+	+	+	+	+	+	+	+	+	+
4. Diethylene glycol	–	–	–	–	–	–	–	–	–	–

"+" conforms to compatabilily; "–" conforms to incompatabilily of components.

It has been established that concentration of permethrin in a plasticizer-insecticide mixture does not practically influence compatibility degree of the components. In usual conditions (at temperature 297 K) complete compatibility is observed only for the composition dioctylphtalate-permethrin. Temperature increase of the mixture up to 338 K leads to dissolution of permethrin in vaseline oil. The the mixtures glycerine-permethrin, diethylene glycol-permethrin are emulsions even at 338 K temperature.

Simultaneously, technological compatibility of above plasticizers with St was investigated. Considarable St swelling in glycerine and diethylene glycol is one of the signs of their compatibility. Besides, films formed from PE-St-plasticizer compositions including above mentioned plasticizers

were distinguished by the greatest homogeneity and strength.

Compatibility of plasticizers and saturated solutions of permethrin in plasticizers with PE was estimated for presence or absence syneresis, that is spontaneous formation of drops or thin deposit of liquid on the film surface. Plasticizer release is known to be one of plasticized plastics disadvantages. However, syneresis can be of prime importance if the plasticizer performs the role of the active additive carrier medium and transports it to a product surface being protected by the film.

For dioctylphtalate and vaseline oil a limit of thermodynamic compatibility (C') with PE at T = 295 K is about 5 mass %. Glycerine is badly compatible with PE. Solutions of permethrin in plasticizers are characterized by lower C' than the initial plasticizers have. At a modifying liquid concentration $C > C'$ its excess is gradually released on the film surface. Syneresis rate grows with increasing liquid phase concentration in a polymeric composition. Nevertheless, the upper range of functional liquid content in the films is limited by 20 mass % value. At a higher concentration strength characteristics of the films sharply impair and do not meet standard requirements to packing films.

An important parameter of technological compatibility of IBF components is their thermal stability at joint processing by extrusion equipment (table 2).

Table 2

Melting points (T_m), temperatures of termodesruction (T_{ts}) and intensive thermodesruction start (T_{its}) of IBF components and their mixtures based on derivatographic analysis

The sample	T_m, K	T_{ts}, K	T_{its}, K
1. PE	387	516	655
2. Starch	—	503	533
3. Glycerine	—	413	—
4. Vaseline oil	—	458	493
5. Permethrin	387	468	513
6. Dioctylphtalate + permethrin	—	435	448
5. PE + starch	383	523	533

Packing films filled with insecticide and biodegradable composition (corn St plastisized with glycerine) can be produced by the slot-hole and hose melt-blowing extrusion methods [1; 11] (fig. 1).

The original film production technique has been patented by V. A. Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus. It is based on thermodiffusion saturation of the inner surface layer of polymeric hose during blowing (below the line of polymer crystallization) by a modifying liquid [7–9]. The liquid is supplied to the mandrel of extrusion head and contacts the polymeric hose which is in a viscous-flow state. Combination of insecticide with the polymeric base proceeds at a rather soft temperature regime (table 3). Thus, functional compositions with low thermal stability can be introduced into the film.

The structure of thus formed films is characterized by the presence a jelly-like modified layer containing insecticidal liquid which is continuously separating from the film due to syneresis. The modified layer gradually transforms across film thickness into a continuous polymeric layer fulfilling barrier functions.

Table 3

Parameters of IBF production process (film thickness ~ 100 mm)

T in zones		T_l,	H_l,	P_m,	v_{extr},
Cylinder	Head	K	mm	MPa	m/s
I — 423 II — 433 III — 453 IV — 463	I — 443 II — 433 at exit — 413	383–393	5–15	12	5×10^{-2}–10^{-1}

T_l, h_l – temperature and height of modifying liquid layer above the mandrel of extrusion head; P_m — melt pressure in the head; v_{extr} — extrusion rate.

By changing of h_l and v_{extr} parameters it is possible to control time of functional liquid contacting with molten polymeric base and to set the modified layer thickness and concentration of introduced into the film insecticide. Production expenses at a given procedure of IBF manufacture are minimal, insecticide is consumed economically during material use due to release mainly from one side of the film, i. e. inwards the packaging.

At slot-hole extrusion an optimum temperature distribution have been determined in the zones

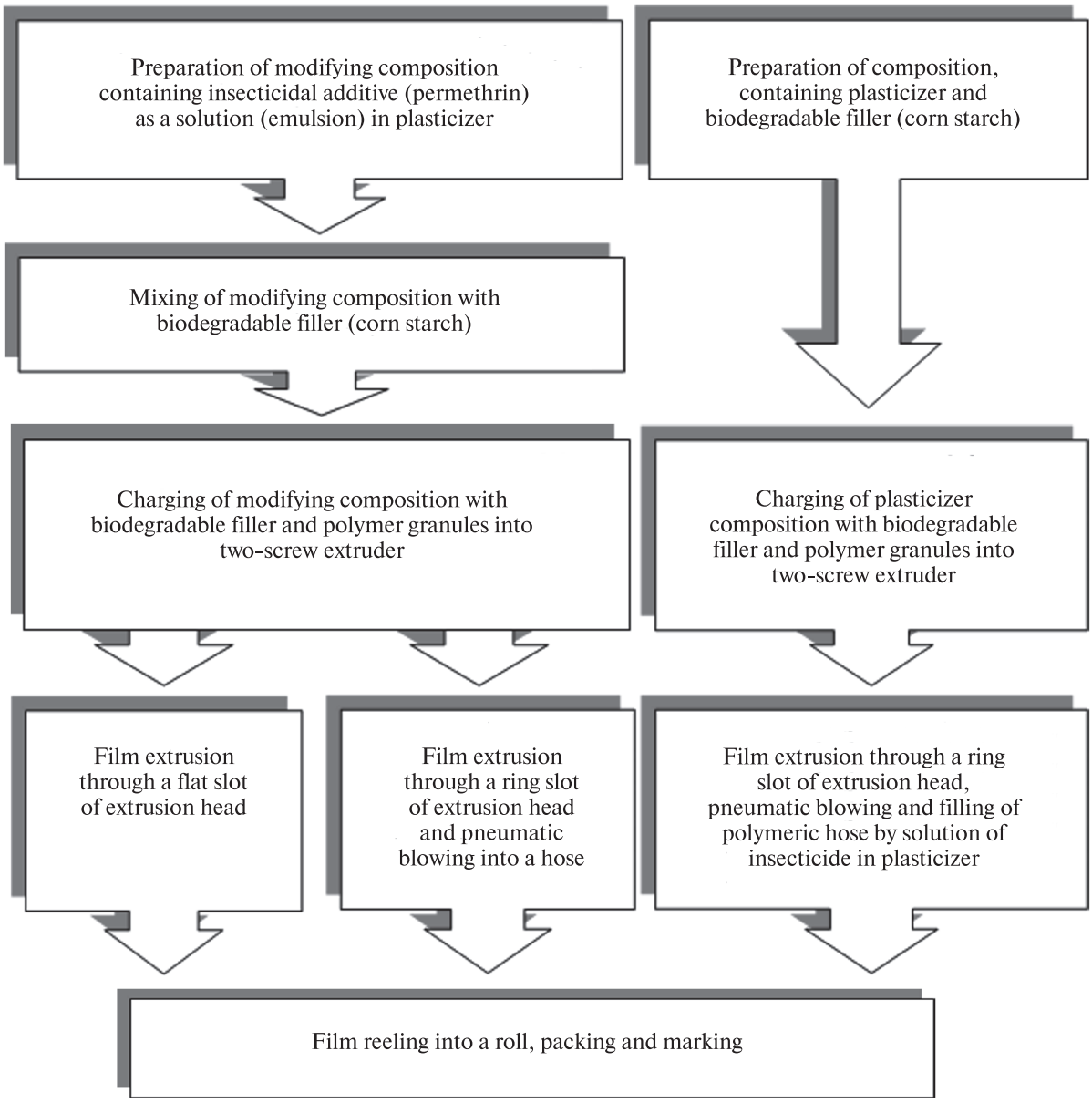


Fig. 1. Technological layout of PE-based IBF production

of extruder: I — 393 K, II — 413 K, III — 423 K, 433 K — at the head exit.

The efficiency of insecticidal action of the film was estimated by the relative number of died moth butterflies *Nemapogon granellus* 3 hours after exposhure in vessels (2 dm^3 volume) together with the samples of insecticidal films. This parameter was calculated according to the formula:

$$E = (n_0 - n_1) \cdot 100 / n_0,$$

where E is efficiency of insecticidal action, %;
n_0 is initial amount of butterflies;
n_1 is amount of alive butterflies after 3 h.

Practically 100 % of butterflies have died after 3 or 4,5 hours of contact with the films containing 20 mass % or 10 mass % of permethrin, accordingly (table 4).

Kinetics and mechanism of film samples destruction have been studied in natural conditions. Samples were placed into an arable soil treated by organic-mineral fertilizers up to 5 cm (aerobic) or 15–30 cm (anaerobic condition) depth and were endured there for 1, 3, 6 and 12 months. Variation kinetics of mass, physico-mechanical characteristics, micro- and molecular structure of film samples removed from the soil was studied using a complex of physical, physico-chemical and microbiological methods.

Biodegradation rate (v, table 4) was estimated in accordance with the following equation:

$$\nu = (m_0 - m_1) \cdot 100 / m_0,$$

were m_0 is initial mass of the sample;
m_1 its mass after 3 months of exposure in soil.

Table 4

Tensile strength (*s*), efficiency of insecticidal action (*E*) and biodegradation rate (*v*) of polymer film samples

Film composition, mass, %			σ, MPa	*E*, %	*v*, %
HDPE	St	Permethrin			
100	0	0	21,3	10	0
100	0	10	20,2	67	0
100	0	20	19,8	99	1
70	30	0	13,3	12	40
70	30	10	12,5	65	43
70	30	20	11,9	98	45
50	50	0	7,3	11	50
50	50	10	6,3	63	52
50	50	20	5,5	97	54

The initial structure of samples underwent substantial changes during tests. Density increase, transparency decrease, elongation at rupture increment were observed for films of non-modified PE. In some cases elongation increment was within 60–150 %. Evidently, it can be the result of secondary crystallization of PE and migration of organic-mineral substances (polymer plasticizers) from the fertilized soil into the polymeric matrix.

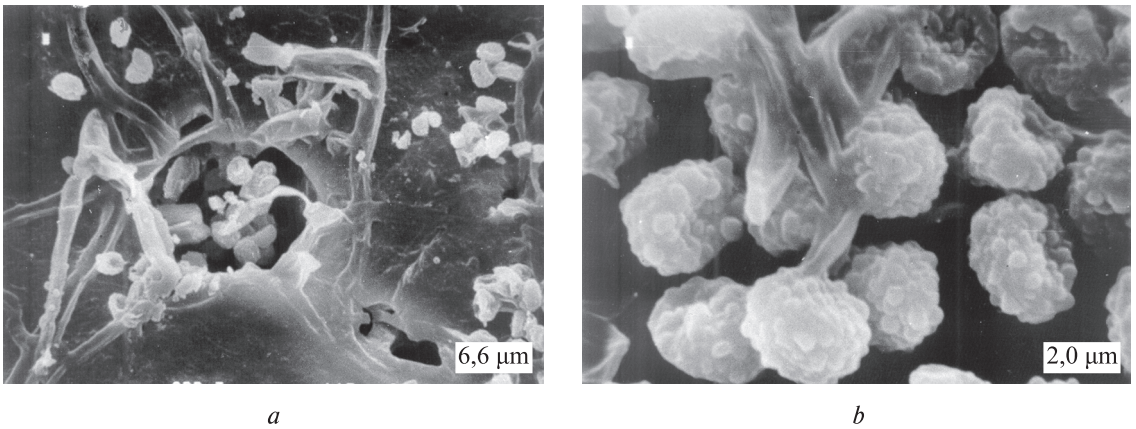
IBF samples underwent even deeper changes. At exposition in soil both in aerobic and anaerobic conditions loss of weight, pore formation, cracking and destruction of the samples took place as well as film fouling by microorganisms. Above changes were visual after a month existence in soil. Degree of film destruction was noted to be proportional to concentration of polysaccharide additive. Tensile strength of composite film samples, in contrast to films of non-modified PE, reduced perceptibly which is an evidence of the beginning of material biodestruction process (table 4).

Strength reduction of composite films is uneven in time. But destruction process of films of different composition proceeds more intensively in anaerobic conditions when microorganism action dominates over weather conditions.

It was established that raised insecticide concentration in the film does not influence essentially strength characteristics of IBF but favours biodegradation (table 4). Besides damages through biodegradation of polysaccharide filler, the additional effect of destruction is caused by structural features of the filled samples. The filler is known to accumulate in less ordered zones of polymer matrix. Moreover, density of macromolecular packing in boundary layers of the "polymer – filler" system is approximately half as much as in the rest volume of disordered polymer phase. Therefore, after filler destruction by microorganisms their free access is eased to a most susceptible to biodegradation part of the polymer.

Interaction of fungi *Aspergillus, Penicillium, Trichoderma* with IBF samples has been investigated by the method of microbiological testing [4; 6; 12]. It has been determined that intensity of mycellium germination of above fungi-biodestructers, their covering film surface, internal penetration and adherence to the samples depend on the presense of polysaccharide additive (St) in the film as well as on conditions and time of its endurance in soil.

This conclusion is confirmed by the results of structural examination of film samples removed from the soil. Electron microphotographs (fig. 2) illustrate enlarged porosity polymeric matrix, characteristic distribution of filaments and conidial heads of fungi in pores of the material as well as accumulations of bacteria cells on film surface.



a *b*

Fig. 2. Electronic microphotographs of film samples with composition PE + St + glycerine + permethrin upon 3 months exposure in soil

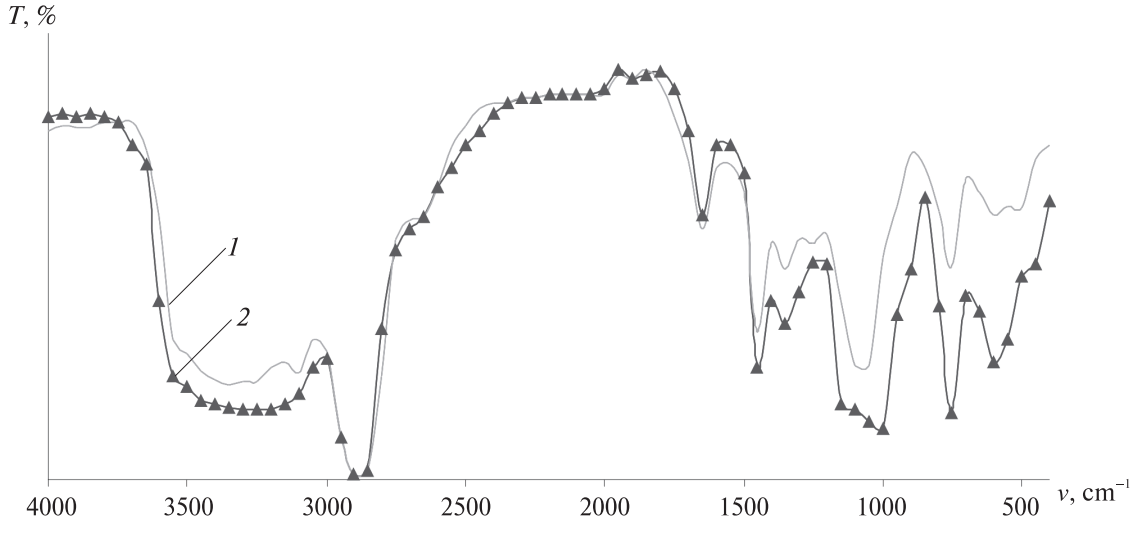


Fig. 3. IR-spectra of film samples containing 45 mass % of St: *1* — before and *2* — after 3 months of exposure in soil

The following changes are observed in IR-spectra of the films in time. Intensity of absorption peaks related to polysaccharide component (at 3200–3400 cm^{-1}, 1000–1200 cm^{-1}) reduces and absorption increases in spectrum regions corresponding to oxidized forms of the polymer (fig. 3).

So, PE based films modified with components of biological origin (St) are subjected to intensive biodegradation in soil. Rate of biodegradation depends on a complex of factors. Presence of biodestructive and insecticide additives in IBF, qualitative composition of soil microflora, weather conditions, depth of material location in soil horizon are of great importance. Microbiological damages occur under the action of metabolism products of fungi and other soil microorganisms. Incecticide incorporated in the film does not possess fungi- and bactericidal effect and favours biodegradation process.

A significant economic, ecological and social efficiency of using the offered composite materials is obvious. Their application in packaging industry will reduce product losses from damage by keratin-eating insects during transportation and storage, will diminish expenses of used packaging recovery and will improve ecological conditions of urban and industrial zones.

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