

DEGRADATION PROPERTIES STUDY OF LDPE AND PLASTICIZED STARCH COMPOSITE BLOWN FILM

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Abstract: The problem of producing polymer materials with accelerated degradation under ambient conditions is particularly relevant today. One of the solutions is forming synthetic – organic polymer composites and the study of properties and peculiarities of their degradation. The study is dedicated to blown films based on low density polyethylene (PE) and thermoplastic starch (TPS) compound, where thermoplastic starch was in situ formed during compounding process. Thermoplastic composite was produced on industrial scale equipment by using standard filler incorporation techniques – through filler masterbatch which was mixed with target polymer on film blowing equipment. Modern modification techniques were used during masterbatch production – incorporation of graft copolymer and viscosity reduction agent as well transition metal catalysis. Corn starch was first plasticized with glycerol and then used in powder form for compounding on twin screw extruder with polyethylene and additives. Thermal and pressure treatment during compounding converts plasticized starch to thermoplastic starch homogeneously incorporated in polyethylene matrix. Properties changes during degradation of various starch polyethylene composites were studied. The influence of incorporation techniques and various modifying additives on the properties of PE/TPS blown films, such as polyethylene and maleic anhydride grafted polyethylene wax were studied. It was established that the introduction of modifiers leads to a decrease in the viscosity of the composites, and to an increase of the strength and technological properties, and facilitated processing. The rheological properties of modified PE/TPS composites allow the processing using the conventional industrial equipment and technological modes. The reason for the high technological and operational properties of the investigated materials is the increased compatibility of the components of composites due to the influence of modifying additives. An estimation of the properties change of the resulting blown films during degradation in different model environments was carried out. It was established that the use of metal catalysis like ferric stearate significantly increases the intensity of degradation of PE/TPS blown films as a result of initiating the degradation of the PE matrix under the effect of environmental factors. Blown films containing catalysis lose relative tensile strain at yield by 80% after 60 days of stay in the soil which is an important proof of degradation. The results obtained will allow producing polymer films with accelerated environmental degradation and compatibility.

Key words: thermoplastic starch, blown film, plasticized starch, ferric stearate, accelerated degradation.

1 INTRODUCTION

A large number of consumer goods made from polymers need to be recycled after use [1]. However, most polymers degrade in the environment for a long period time, which focuses attention to the production of biodegradable materials [2, 3]. The household products made of polymer materials should quickly degrade after their usage under the ambient environmental conditions [4]. One of the ways to produce such materials involves the introduction of special additives into synthetic polymers accelerating the degradation of polymer macromolecules. For these purposes, polysaccharides, generally starches, as well as oxo-additives [5] are widely used. Another option is the use of bio derived or based polymers as PLA, PCL, PBAT, but for the Ukrainian economy at the present stage it is still expensive.

Presently, the methods of reactive extrusion of polymers are being intensively introduced in the industry [6], thus, the technology of chemical modification of polyethylene (PE) like bonding of the functional macromolecules in the viscous state with polar vinyl monomers (maleic anhydride, itaconic acid, etc.). Modified this way, PE contains active groups in macromolecules and has an enhanced compatibility with polar polysaccharide filler that causes intensified interphase interactions [7].

The research should be considered relevant as it is aimed at finding and developing new ways to accelerate the expansion of synthetic polymers, in particular of polyethylene.

2 ANALYSIS OF LITERATURE DATA AND PROBLEM STATEMENT

The main large group of polymeric materials is composites with synthetic thermoplastics and natural polymers. The insertion of starch in PE is known as a technology for improving the degradation of products based on PE. However, it should be noted that despite a great deal of work, low compatibility of bioactive additives with PE is a serious problem.

The scientists [10] investigated the explicit dependence of rheological, physical and mechanical properties, time of biodegradation of a polymer on the content of starch. The obtained results indicate that the increase of the starch percentage in the composites is accompanied by reduction of the melt flow index, tensile strength and strain of the composite.

According to the authors [11], the greatest disadvantages of the technology of combining PE and starch are the low mechanical characteristics of the resulting composites, the degradation of starch at processing temperatures, boiling of starch, poor appearance, and sensitivity to moisture. In addition, the films obtained are not transparent that limits the scope of use of such composites, especially as packaging materials, as described in detail further [12].

Since adding of powdered pure starch into PE has a number of shortcomings as highlighted by the authors [13], the blending plasticized starch with PE is a modern approach to the production of polymeric materials with a prolonged service life on the basis of synthetic polymers, the purpose of which is to overcome these shortcomings. The term "plasticized starch" refers to a blend of starch with glycerol as a plasticizer and glycerol monostearate (GMS) as lubrication agent [14].

In the study it is stated that the transformation of plasticized starch particles in thermoplastic starch (TPS) occurs during the processing of PE blend on the extrusion equipment under the effect of pressure and temperature. In this case, the starch particles (globules) are distributed in the polymer matrix and isolated from each other by the polymer layer. The processes of transforming the crystalline phase into amorphous proceed in isolation at the level of starch globules [15].

The authors [16] consider in detail the technology of obtaining TPS by thermo-mechanical degradation of pectin component of starch in the process of extrusion processing. TPS obtained from native starch in its pure form does not possess a complex of properties necessary for processing of the packaging materials. TPS is characterized by low tensile strain, moisture sensitivity and very high melt viscosity.

In the study [17] it was established that addition of compatibiliser like PE-itaconic acid graft copolymer into PE/plasticized starch blend, a more homogeneous structure of composite films is formed that is characterized by the absence of striking interphase boundaries causing an increase in the technological characteristics of film materials (tensile strain at yield, elasticity and biodegradation). The possibility of using compatibilisers in the PE/plasticized starch system is confirmed by the improvement of rheological, physical, mechanical and performance indicators.

It should be noted that most research in this topic is focused on laboratory scale samples produced on laboratory equipment. The main experimental objective of current study is to introduce plasticized starch technology in industrial scale production process with application of industrial filler incorporation methods.

Thus, experiments in this direction are promising and relevant.

3 PURPOSE AND OBJECTIVES

The aim of the work is to study the properties and degradation of blown films based on PE and TPS formed in industrial film production process followed by compounding and film blowing. To achieve this goal, the following tasks had to be solved:

- to study the influence of various modifiers on the properties of blown films PE/TPS;
- to study the degradation of PE/TPS blown films in various model environments.

4 MATERIALS AND METHODS

The following raw materials were used:

LDPE of type 15803-020 (MFI 2.0-2.4 g/10 min); corn starch (DSTU 4286: 2004); plasticizer - glycerol pharmacological grade, lubricant - glycerol monostearate (GMS).

Modifiers: polyethylene wax (PW-200), maleic anhydride (MA) grafted polyethylene (MA-g-PE) produced by the solid-phase synthesis method according to the technique described in [18]. As additive for accelerating the degradation of PE ferric hydroxy-stearate II (Fe stearate) synthesized by reaction in water solution was used as component of starch composition and PE matrix.

The MFI of PE was measured in accordance with ISO 1133 at the temperature $190 \pm 0.5^\circ\text{C}$ and the weight of 2.16 kg. MFI of TPS was measured at a load of 21.6 kg. The preheat period of material is 5 min. The density of the composites was determined by the hydrostatic weighing method according to GOST 11035.2-93. Moisture absorption was determined as change in the mass of the specimen for 24 hours at 23°C for ISO 62 (ASTM D570).

Tensile strength was determined according to ASTM D638. Statistical processing of experimental data was carried out using standard methods. [19]. To evaluate the degradation, the film samples were boiled in water and alkali solution, aged in the soil over a period of time. The changes in mass and mechanical properties were measured.

The microstructure of the samples was studied using optical MIN-8 ($\times 200$) and electronic GEOL GSM-35 microscopes. Structural changes were estimated by the IR spectroscopy method on the TENZOR-25 FTIR instrument in the absorption frequency range of $500\text{--}4000\text{ cm}^{-1}$. The optical properties of the films were measured by a photoelectric colorimeter KFK-2-UHL4.2. The index of integral light transmission at the films thickness of $0.2\text{--}0.3\text{ mm}$ was calculated.

Preparation of powdered plasticized starch was carried out in the two-shafted open mixer at room temperature, mixing time 30 min, at 150 rpm. The standard contents of the plasticizer and lubricant for thermoplastic starch were used [16]. Glycerol and GMS were mixed using a magnetic stirrer at $T=90^{\circ}\text{C}$ until complete dissolution of GMS in glycerol. The blend of glycerine and GMS was added to starch after drying at $T=80^{\circ}\text{C}$ for 2 hours for final moisture content of 12% in the ratio of starch: 80:20.

Standard industrial approach of the introduction of plasticized starch into a polymer matrix was used. There are two common methods for incorporation such filler in to processing stream – buy production of ready to use compound or a masterbatch (concentrate) as part of composition. The compound can be processed in to article without any additional steps and offers best known mixing quality. The masterbatch method involves compound diluting with resin before processing and is commonly used in industry.

When preparing blends, the method of masterbatch was used since it is the simplest and widely used on industrial scale. The concentrate of plasticized starch with PE was obtained by preliminary mixing the resulting plasticized starch with PE powder in a high-speed Henschel mixer. The resulting powder mixture was processed on a laboratory twin-screw extruder $D=22\text{ mm}$, $L/D=40$ at the average processing temperature of 170°C .

Granular TPS and TPS film were obtained by the method [20] at temperature of 130°C on a single-screw extruder.

TPS masterbatches were mixed with LDPE grade 15803-020 in the ratio of 50:50 during the production of blown films. The diameter of the blowing die was 40 mm . Blow ratio was 2.5. The diameter of the extruder screw is 25 mm , the ratio $L/D=28$. Average processing temperature is 180°C . Target film samples thickness was $50\pm 3\text{ micron}$.

5 PROPERTIES OF TPS COMPOSITE BLOWN FILM

As a result of numerous experiments, more than 30 different concentrate recipes were tested. For further studies recipes with satisfactory rheological and technological properties were listed for evaluation. For comparative studies, a few numbers of representative compositions were selected for masterbatch production with planned TPS content of 50%, which is listed in Table 1.

The pure PE film produced in a same condition with the samples and TPS film produced by flat die extrusion was used for comparison.

The following masterbatches was produced:

№1 – (St/PE) powdered pure starch with polyethylene;

№2 – (TPS/PE) - powdered plasticized starch with polyethylene;

№3 – (TPS/PE/PE-g-MA) powdered plasticized starch with polyethylene and PE-g-MA compatibiliser;

№4 – (TPS/PE/PW) powdered plasticized starch with polyethylene and PE wax as wetting and dispersion additive;

№5 – (TPS/PE/FeSt) powdered plasticized starch with polyethylene in which the prodegradant ferric stearate was pre mixed with polyethylene component;

№6 – (TPS/FeSt/PE) powdered plasticized starch with polyethylene in which the prodegradant ferric stearate was pre mixed with starch composition.

Masterbatches were produced by strand granulation with water cooling, so after production step they were dried in air circulating oven and stored in water vapor barrier bags. After production general rheological and technological properties of the masterbatches were measured (Table 2).

Table 1 Composition of masterbatches and samples

№	Component	PE	TPS	Masterbatch composition					
				№1	№2	№3	№4	№5	№6
				Weight [%]					
1	PE 15803	100	–	50	50	50	50	49.8	50
2	PE-g-MA	–	–	–	–	5	–	–	–
3	Starch composition	–	100	–	50	45	40	50	50
	Starch	–	80	50	40	36	32	40	39.6
	Glycerine	–	19	–	9.5	8.55	7.6	9.5	9.5
	GMS	–	1	–	0.5	0.45	0.4	0.5	0.5
	Fe stearate	–	–	–	–	–	–	–	0.4
4	PE wax	–	–	–	–	–	10	–	–
5	Fe stearate	–	–	–	–	–	–	0.2	–

Table 2 General properties of granular masterbatches and samples

Properties	PE	TPS	№1	№2	№3	№4	№5	№6
MFI [g/10min]	2.6	0.15*	1.0	1.3	4.2	7.5	1.3	1.2
Density [kg/m ³]	925	1419	921	929	930	931	928	929
Bulk density [kg/m ³]	570	680	620	628	630	650	630	629
Water vapor absorption [%]	0.02	2.61	0.91	0.21	0.12	0.08	0.20	0.21

*MFI at 21.6 kg

Table 3 Film samples composition obtained from concentrates

	Component	PE	TPS	Film sample					
				№1	№2	№3	№4	№5	№6
		Weight [%]							
1	PE 15803	100	–	75	75	75	75	74,8	75
2	PE-g-MA	–	–	–	–	2.5	–	–	–
3	Starch composition	–	100	–	25	22.5	20	25	25
	Starch		80	25	20	18	16	20	19.8
	Glycerine		19	–	4.75	4.28	3.80	4.75	4.75
	GMS		1.0	–	0.25	0.22	0.20	0.25	0.25
	Fe stearate		–	–	–	–	–	–	0.20
4	PE wax	–	–	–	–	–	10.	–	–
5	Fe stearate	–	–	–	–	–	–	0.20	–

Table 4 The main properties of films obtained from concentrates

Properties	Samples		Composite film samples					
	PE	TPS	№1	№2	№3	№4	№5	№6
MFI [g/10min]	2.20	0.15*	1.1	1.6	5.4	6.5	1.6	1.7
Moisture absorption [%]	0.01	10.0	2.60	1.50	1.00	0.80	1.40	1.45
Density [kg/m ³]	925	1419	918	928	925	930	927	929
Tensile strength [MPa]	16.0	9.4	3.6	6.8	10.2	5.8	6.9	6.8
Elongation at break [%]	600	34	28	151	167	82	162	135

*MFI at 21.6 kg

Water vapor absorption of granular masterbatches and samples were measured at room temperature, 80% RH after 72 hour of open air storage. The results indicate the importance of vapor barrier packaging for such compounds.

MFI data show reduction comparative to native resin, highest reduction in composition of pure starch and less with plasticized starch. Visual appearance of composition #1 is milky white; all other composition is semi-transparent which can be potentially colored in desired way more freely.

Masterbatches were mixed with PE resin and processed in blown film, properties of film samples are listed in Table 3.

MFI, deformation-strength parameters as well as the degradation kinetics of obtained films in soil and stimulated medium were investigated (Table 4).

The film №1 has low quality surface appearance (matte surface) despite composition was produced on twin screw extruder. Other composition has much better surface gloss especially composition containing PE wax and compatibiliser which is valuable for film end use application in packaging area. The film №2 has a smooth outer surface, homogeneous in composition and characterized by slight turbidity. The film №3 is externally smooth with a glossy surface, homogeneous in composition and

more transparent compared to the film №2 that may indicate a better compatibility of components of the blend. Improvement of mixing of components with the introduction of a compatibiliser MA-g-PE can be explained by the chemical interaction between the starch and PE molecules under the influence of high temperatures and shear during formation.

As for the film №4, PE wax reduces the viscosity of the system by wetting the particles of starch that provides more homogeneous distribution of components in the polymer volume. The appearance and properties of films №5 and №6 are similar to film №2 and ferric stearate is well dispersed in a polyethylene environment.

When PE-g-MA and PE wax are introduced in the films №3 and №4, MFI increases compared to the film №2 which leads to a better processing of blends. These films are sufficiently resistant to water; the degree of water absorption does not exceed 1.0%. This is of fundamental importance, since if the film is water resistant, thus when the film material enters the conditions of intense moisture, the physical and mechanical properties may deteriorate. Low degree of water absorption leads to the expansion of areas of the application of the films, moisture absorption of film from TPS is almost 10%.

It was established that the strength of the film №3 samples compared with the initial PE (see Table 4) decreases slightly and the strength of the films №2 and №4-6 is lower than the index of the initial PE and TPS. In case of the film №4 with a compatibiliser PE wax, there is a decrease in the tensile strength and relative elongation compared to other films because wax reduces intermolecular interaction in the system. It should be noted that the relatively high strength ratios in films with MA-g-PE compatibiliser confirms the improvement of the compatibility of the blend components.

In accordance with the established tasks, the kinetics of moisture absorption of the films in a humid environment was investigated. The obtained results are presented in the form of corresponding graphs of mass change of samples depending on their duration time in a humid environment (Figure 1).

Being under conditions of moisture, in all the samples, the growth of moisture absorption associated with the swelling of starch in the surface layers of the film is initially observed, after then the moisture level was stabilized. The maximum equilibrium moisture absorption of films №3 and №4 is 1.5 times lower than of the films №2, №5 and №6, since the compatibiliser improves the compatibility of the blend components and reduces the access of moisture to the starch component.

In accordance with the research objective, the ability of the films degrade was studied. For this purpose, the behavior of property change in various mediums was studied. There was monitored the weight change of the samples, which were subjected to boiling in water and 0.1 N NaOH solution for 24 hours. The weight of the samples was determined in weight %. The results obtained are presented in the Figures 2 and 3.

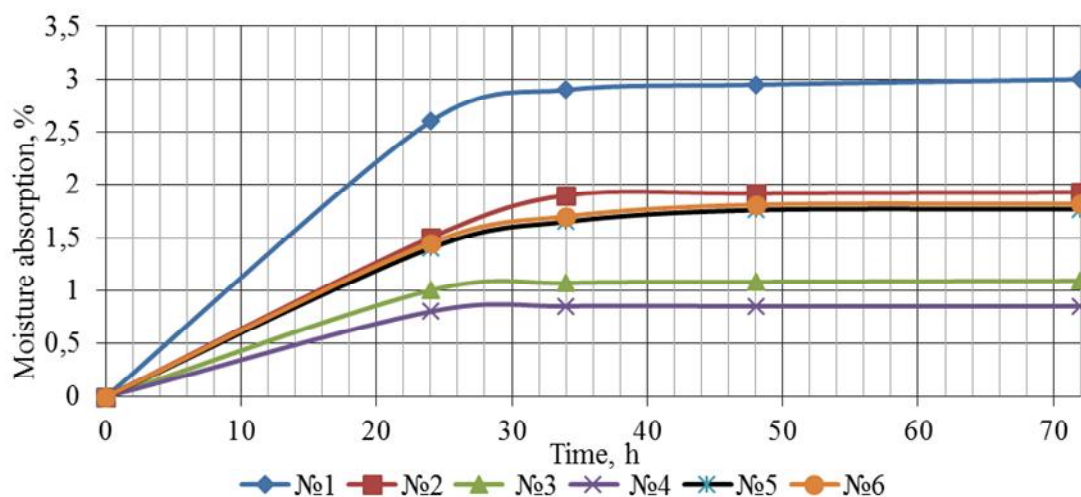


Figure 1 Dependence of moisture absorption of film samples №1-6 on duration time humid medium

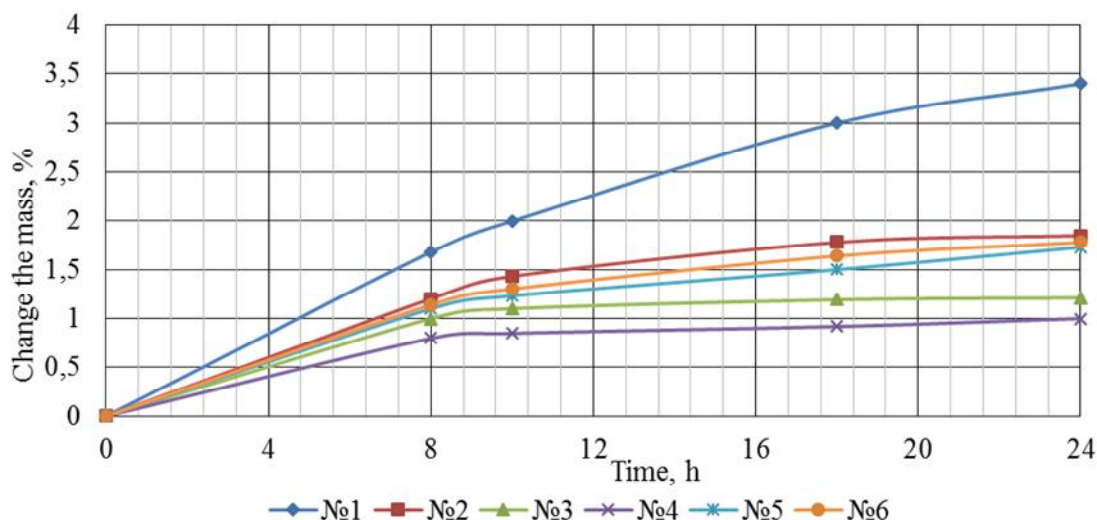


Figure 2 Mass changes of films samples №1-6 during boiling in water

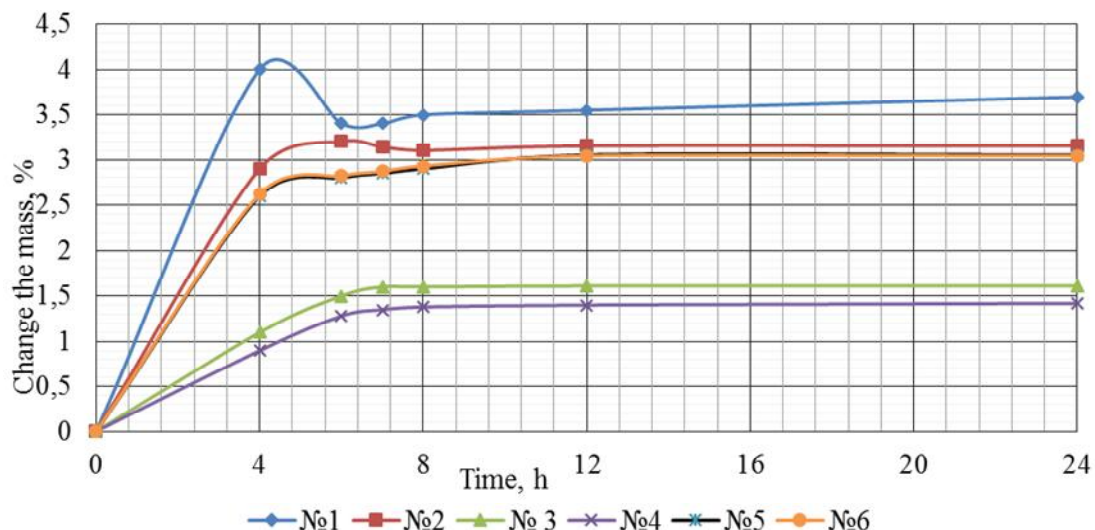


Figure 3 Mass changes of films samples during boiling in a 0.1 N solution of NaOH

When boiling in water all samples of films, there is a process of mass growth due to the swelling of the starch component. The comparative analysis of the films behavior during boiling in an alkaline medium (Figure 3) showed the following: the mass change of film samples №3 and №4 is almost two times less than for the films №2, №5 and №6, indicating that the starch is washed off intensively from films surface that do not contain a compatibiliser.

For film №1 there is a spike of a mass change after 4 hours of boiling as the possible result of a significant swelling of starch in alkaline solution. Further reduction of mass is related to the washing of starch from film №1.

The mechanical properties of the films after boiling in the stimulated medium were also determined.

The tensile strain at yield (δ) and tensile strain at break (ϵ) before and after boiling of films in water and 0.1 N NaOH solution are shown in Table 5.

The microstructure of samples of the film №3 was also studied before and after boiling hydrolysis using an optical microscope MIN-8 ($\times 200$).

In the Figure 4 one can see a clear boundary between the phases of the PE matrix - the starch grain in the initial film (a), indicating a relatively low compatibility between the matrix and the starch.

Table 5 Mechanical characteristics of films before and after 24 h boiling in different medium

Film	Initial values		After boiling in water		After boiling in 0.1N NaOH solution	
	δ	ϵ	δ	ϵ	δ	ϵ
PE	16.0	600	16.0	600	15.8	597
№1	3.6	28	3.0	18	2.2	18
№2	6.8	151	6.4	125	4.2	98
№3	10.2	107	9.9	94	7.9	90
№4	8.8	82	7.6	72	5.8	31
№5	6.9	162	3.6	61	2.8	76
№6	6.8	135	3.9	72	3.3	81

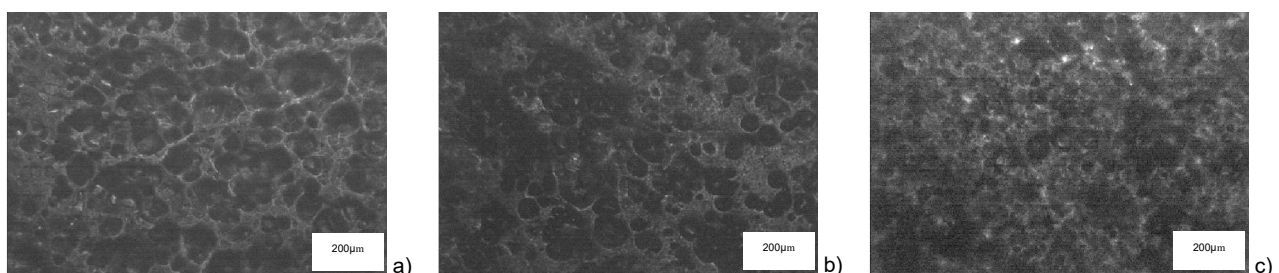


Figure 4 Microstructure of the film №3, a) before hydrolysis; b) after hydrolysis in water; c) after hydrolysis in 0.1 N solution of NaOH

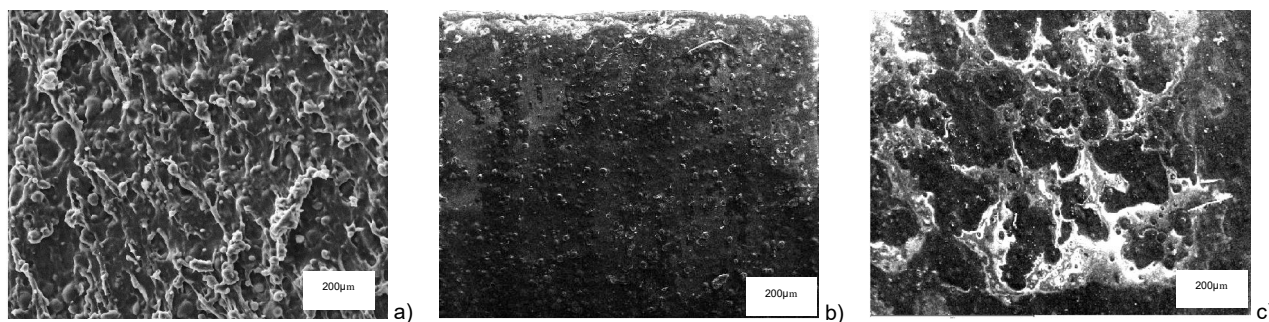


Figure 5 SEM images of films with different composition: a) TPS film; b) film №3; c) film №3 after boiling in 0.1 N solution of NaOH

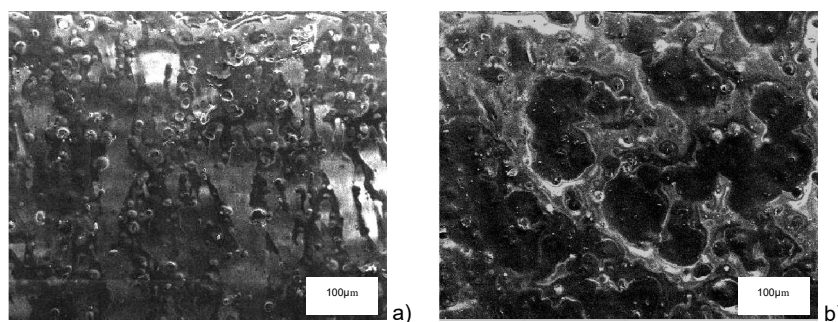


Figure 6 SEM images of film №3, an increase by 100 µm: a) film №3; b) film №3 after boiling in 0.1 N solution of NaOH

Boiling in distilled water (b) causes minor changes on the surface of the film due to partial starch washing off. After boiling in a 0.1 N solution of NaOH (c), the boundaries of the phase separation become more blurry, indicating a process of more intense washing of starch from the surface layers of the film. The starch in the inner layers remains encapsulated in the PE. In Figures 5 and 6 are SEM images of the films with different composition.

Figure 6 shows the SEM images for film №3 before and after boiling in 0.1 N solution of NaOH.

As for the film sample №3, the effect of the alkalis is characterized by a smoother surface, without cavities, and after boiling, there is sight of porous structure, indicating the formation of erosion and washing of starch from the surface layers.

From the figures it is seen that the structure of the polymer material is heterogeneous: the starch grains are permeated with the "threads" of the polymer binder and in the surroundings of each grain (or agglomerate of grains) there is a shell formed by a film based on synthetic PE. In addition, there is a fairly large number of pores in the material structure that makes the material potentially accessible to the effect of moisture and microorganisms.

Infrared spectra of the films are presented in Figure 7. For the study, film №3 and film №3 after boiling in 0.1 N solution of NaOH and PE and TPS films were selected for comparison. On spectra (samples 1-3), in the frequency range $1302\text{--}1076\text{ cm}^{-1}$, there are characteristic peaks of starch absorption [13]. The introduction of plasticized starch into PE leads to a peak shift at a frequency of 888 cm^{-1} to the frequency range of $861\text{--}853\text{ cm}^{-1}$. The intense absorption peak in the range $3400\text{--}3100\text{ cm}^{-1}$ corresponds to the -OH groups [21].

The mark of PE degradation is absorption peak at a wavelength of 1760 cm^{-1} on the IR spectrum. After boiling of the film №3 in 0.1 N solution of NaOH, no significant changes were noted. Therefore, it is expedient to introduce in the composition of TPS/PE films degradation catalysis ferric stearate II, which initiates the decomposition of PE matrix under the influence of light, oxygen and temperature (Figure 8). In Figure 8, there is an intense absorption and at a wavelength of 1760 cm^{-1} (curve 3), indicating PE component degradation.

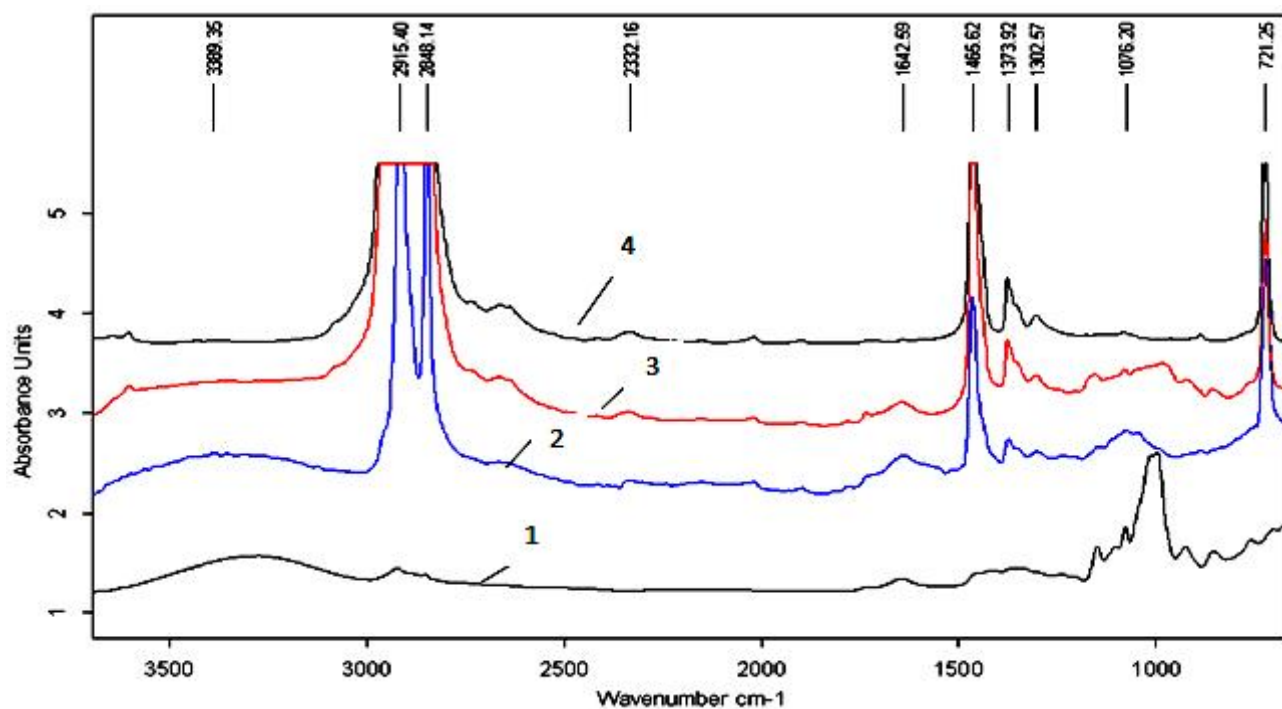


Figure 7 Infrared spectra of films: 1) TPS film; 2) film №3 after boiling in 0.1 N solution of NaOH; 3) film №3; 4) PE film

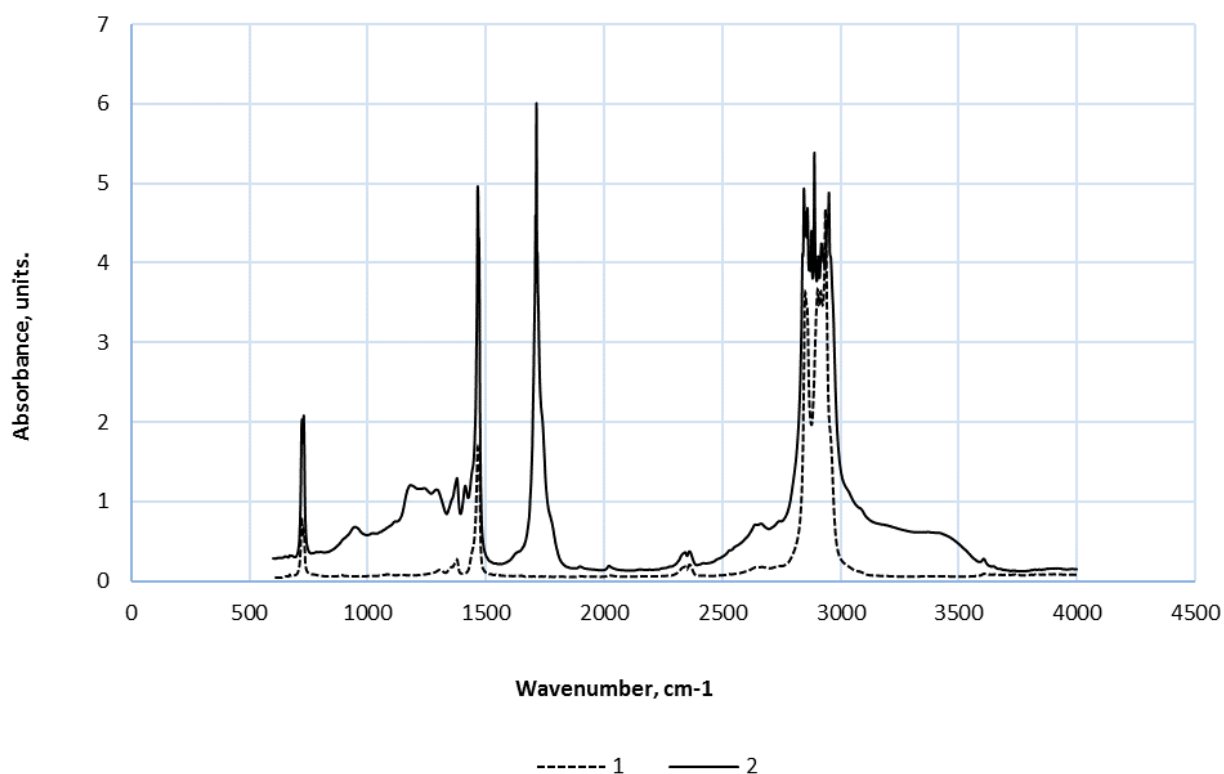


Figure 8 IR film spectra: 1) PE film; 2) film №5

Loss of the films mass after incubation in the soil (cultivated soil, pH=6.5, temperature 20-25°C, humidity 60%) is presented in Table 6.

Table 6 Change in the mass of film samples after incubation in soil

Films	Change the mass [%]		
	20 days later	40 days later	60 days later
№1	+3.6	-1.2	-4.6
№2	+3.7	-1.4	-4.9
№3	+1.9	+0.5	-1.7
№4	+1.6	+0.3	-1.0
№5	+3.8	-1.5	-6.7
№6	+3.6	-1.6	-7.0

After 20 days of incubation of films in the soil, the mass increases as a result of swelling of the starch component. After 40 days of exposure, they have signs of biodegradation of starch component 10-15% of the film area. After 60 days of incubation, a decrease in the mass of the films is noted as a result of the biodegradation of starch.

The low ability of the investigated films to biodegrade in the soil may be due to the following. It is known that the biodegradation of films in soil is mainly on the surface enriched with starch. With low content of starch (up to 20%), its particles remain encapsulated in the polymer and therefore are hard to reach for the microorganisms. The process of biodegradation is slowing down. The second reason that reduces the ability of films to biodegrade is an increase of the barrier properties due to the presence in a system of a compatibiliser or a wax. It should be noted that the initial PE was not biodegradable throughout the study period.

Analysis of the results of studies of the mechanical properties of films after incubation in soil showed that after 60 days in the soil for films №5 and №6, the relative tensile strain at break is significantly reduced by 80-88%. This is due to the acceleration of the PE matrix degradation by the degradation catalysis and the diffusion of moisture into the inner layers of the film that is a characteristic feature of the polymer film degradation (Table 7).

Table 7 Mechanical characteristics of films after incubation in soil

Film	initial		20 days		40 days		60 days	
	δ	ϵ	δ	ϵ	δ	ϵ	δ	ϵ
PE	16.0	600	16.0	600	16.0	600	16.0	580
№1	3.6	28	3.3	16	2.9	16	2.4	13
№2	6.8	151	6.2	148	5.2	121	4.7	108
№3	10.2	107	9.5	93	9.3	60	8.5	51
№4	5.8	82	5.5	78	5.3	61	4.9	49
№5	6.9	162	5.6	89	4.4	42	3.1	20
№6	6.8	135	6.0	84	5.0	48	3.4	28

Optical surface images of films at different stages of incubation in the soil (before incubation, after 20 days and 40 days) are presented in Figure 9 (a, b, c - respectively).

The samples of films №3 (upper row) and №4 (bottom row) were studied. It is evident that two-phase structure is characteristic for both types of films. However, the morphology of the samples varies. In the film №3 mainly observed individual grains, starch particles which are fairly evenly distributed in the volume of the PE matrix. The structure of such film is homogeneous that, apparently, determines its higher mechanical performance.

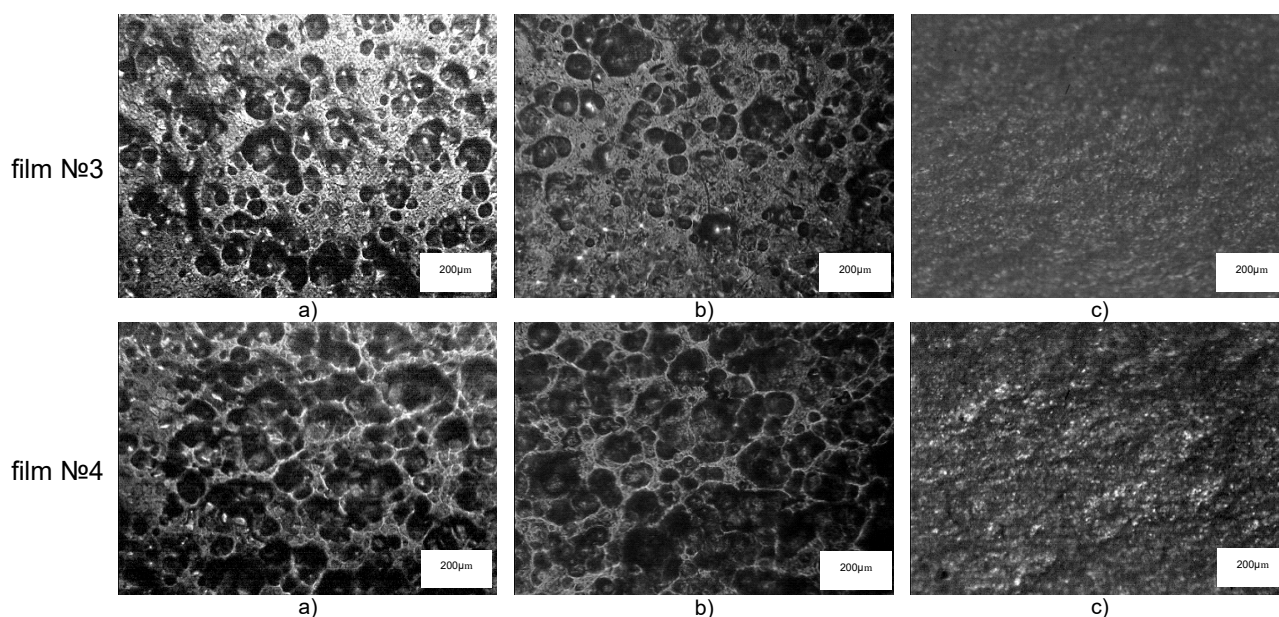


Figure 9 Surface images of films ($\times 200$) with different incubation duration; a) the original sample; b) after 20 days; c) after 40 days

For the film №4 a structure with significant defects is observed. This is due, first of all, to the aggregation of starch particles as they have varying lengths, and there is an uneven distribution of these aggregates in the PE matrix. Such structural features may indicate a low compatibility of the PE matrix with the starch particles.

After 20 days of incubation in the soil in the structure of the film №3 there is a decrease in the number of starch particles, that is, their biodegradation begins in the surface layers of the film. As for film №4, the process of biodegradation is slower; there is only a partial degradation of starch aggregates and appearance of individual grains of a bio component.

After 40 days of stay of both types of films in the soil, their structure undergoes some changes. The boundaries between the phases are blurred or virtually absent. It can be assumed that the process of biodegradation of starch in the surface layers of the film is almost complete. Removing starch from the outer layers of the films leads to a reduction in pores and defects associated with starch particles that extend to the surface of the samples. The stiffness of the films decreases, a smoother surface appears. Further, the destruction process will occur due to starch particles that are already located in the inner layers of the film. This process is much slower, since the access of microorganisms inside the film is much smaller than that to the surface layers.

Optical properties of films were studied. The index of integral light transmission at the thickness of films combined layer 0.1 mm (Table 8) was calculated.

Table 8 Optical properties of films

Films	Coefficient of integral light transmission [%]
PE	88
TPS	64
№1	52
№2	67
№3	83
№4	79
№5	68
№6	69

It was found that the samples containing MA-g-PE and PE wax are more transparent than the original ones which is a technologically favorable factor, but on the other hand, they are less prone to degradation in the environment.

6 DISCUSSION ABOUT THE RESEARCH FINDINGS

Starting from general idea of researching the modern methods of production of degradable PE films, an attempt to introduce degradable filler, like native starch into PE matrix, was made. The obtained film (the film №1) was characterized

by an uneven distribution of the filler in the matrix, low mechanical properties and transparency.

The next step was to obtain films based on a mixture of PE with plasticized starch (film №2). In this case, there was a noticeable improvement in the structure of the film, smooth surface, partial transparency, but mechanical properties were still quite low.

Therefore, the next stage is the introduction of modifiers which due to their compatibilising effect of various nature, allow to improve the mechanical properties of the films obtained (the films №3 and №4). In addition, MA-g-PE acts as chemical compatibiliser, due to the interaction of reactive functional groups with hydroxyl groups of starch that positively affects the strength of the resulting film. PE wax acts as a physical compatibiliser i.e. lubricant and viscosity regulator of the PE-plasticized starch system improving production effectiveness while processing, although the tensile strain at yield and tensile strain at break in this case are somewhat lower compared to film №3.

All the results of experiments allowed to obtain films with acceptable for end application mechanical properties, good production effectiveness, but not significant accelerated degradation, since the degradation and washing of starch was observed mainly in the surface layers of films. Therefore, it was decided to introduce another modifier into the developed system - degradation catalysis for the PE matrix ferric stearate II (the films №5 and №6) which greatly accelerates the process of joining oxygen to PE macromolecules, and enhance oxidative degradation. The result of its action is the intensification of the degradation processes of the PE matrix under the influence of light or temperature [15]. Thus, as a result of a series of experiments, it was possible to obtain a blown film that is capable of accelerated degradation under the ambient conditions and can be used to make a wide range of packaging materials.

7 CONCLUSIONS

1. The influence of various modifiers on the properties of PE/TPS blown films was studied. It was established that the use of compatibilisers allows to improve the technological properties of the films, transparency through the improvement of the compatibility of the components. There is an increase in the mechanical properties of the film №3 containing MA-g-PE modifier in 1.5 times and a decrease in moisture absorption by 30% compared to the unmodified film №2 (a blend of polyethylene with plasticized starch) due to the encapsulation of starch in the inner layers of the film. The film №4 containing PE wax as modifier has a lower moisture absorption of 47% and a higher index of integral light transmission (79%) compared to the film №2 (67%).

2. The peculiarities of the degradation of PE/TPS blown films in different stimulated mediums were studied. It was found that the ability to accelerated degradation in the environment for the films №3 and №4 is observed predominantly in the surface layers. For the film №3 after being in the soil, there is a decrease in tensile strain at yield by 17% and of tensile strain at break by 52%. For the film №4, respectively, 16% and 40%. The films №5 (a blend of polyethylene with plasticized starch and ferric stearate introduced into polyethylene) and №6 (a blend of polyethylene with plasticized starch and ferric stearate introduced into starch) after incubation in the soil for 60 days, 50 to 55% lose tensile strain at yield and 80-88% - tensile strain at break. Such significant losses of mechanical properties of films are due to the presence in them of a ferric stearate II, which initiates the degradation of the polyethylene component and promotes the degradation of starch in the inner layers of the film.

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