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Influence of modified functional additives on the degradable properties of polyethylene

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The degradability of polyethylene (PE) compositions with binary functional additives based on polyvinyl alcohol (PVAL) modified with soybean oil (SO) or glycerol (Gly) at a concentration of 1–5 wt.% is investigated. The degradation ability of samples is evaluated by the changes in their physical and mechanical characteristics under UV-irradiation and biological factors of the soil within 120 days; also mass-spectrometry was used to analyze the spectrum of ionic fragments, their number, and the intensity. It has also been established that the addition of soybean oil and binary functional additives based on modified PVAL with SO and Gly leads to an increase in the initial strength of the compositions by 19.5–85 % compared to the original PE; while, after the exposure to UV-irradiation and soil biological factors, the strength of the compositions is significantly reduced due to destructive processes. The mass-spectrometric study of the compositions showed that due to functional additives containing SO, Gly and PVAL, structural changes occurred in PE increase degradability under the influence of destructive factors.

Keywords: polyethylene, degradability, soybean oil, polyvinyl alcohol, glycerol, mass-spectrometry.

Ефективність впливу модифікованих функціональних добавок на деградабельні властивості поліетилену. *Т.В.Дмитрієва, С.К.Кримовська, В.І.Бортницький, С.М.Кобилінський, С.В.Рябов*

Досліджено деградабельність композицій поліетилену (ПЕ) з бінарними функціональними добавками на основі полівінилового спирту, модифікованого соєвою олією (СО) або гліцерином (Гл) у концентрації 1–5 мас. %. Здатність зразків до деградації оцінювали за змінами їх фізико-механічних характеристик, що відбуваються під дією УФ-опромінення та біологічних факторів грунту упродовж 120 діб, а також методом мас-спектрометрії за спектром іонних фрагментів, їх кількості, та інтенсивності. Встановлено, що введення добавок соєвої олії та бінарних функціональних добавок на основі модифікованого СО і Гл полівінилового спирту призводить до підвищення міцності композицій порівняно з вихідним ПЕ на 19,5 і 85 %, натомість, після дії УФ-опромінення і біологічних факторів грунту внаслідок деструктивних процесів, їх міцність істотно знижувалася. Мас-спектрометричними дослідженнями зразків композицій доведено, що за рахунок введення функціональних добавок, які містять СО, Гл та ПВС відбуваються структурні зміни в ПЕ, що пришвидшує його деградабельність під дією деструктивних факторів.

Исследована деградабельность композиций полиэтилена (ПЕ) с бинарными функциональными добавками на основе поливинилового спирта (ПВС), модифицированного соевым маслом (СМ) или глицерином (Гл) в концентрации 1–5 мас. %. Способность к деградации образцов оценивали по изменениям их физико-механических характеристик, которые происходят под действием УФ-облучения и биологических факторов почвы в течение 120 суток, а также методом масс-спектрометрии по спектру ионных фрагментов, их количеству и интенсивности. Установлено, что введение добавок СМ и бинарных функциональных добавок на основе модифицированного СМ и Гл поливинилового спирта приводит к повышению прочности композиций сравнительно с исходным ПЕ на 19,5–85 %, тогда как после действия УФ-облучения и биологических факторов почвы, вследствие возникновения деструктивних процессов, их прочность существенно снижалась. Масс-спектрометрическими исследованиями образцов композиций установлено, что за счет введения функциональных добавок, которые содержат СМ, Гл и ПВС, происходят структурные изменения в ПЕ, что приводит к ускорению его деградабельности под действием деструктивных факторов.

1. Introduction

Polyethylene (PE) is a popular thermoplastic material used in various packaging industries due to its high mechanical properties. However, this polymer poses significant environmental problems due to its chemical stability, which leads to the accumulation of solid waste. The main ways to solve the problem of polymeric waste after their collection and sorting are recycling and subsequent use, as well as the possibility of decomposition under the influence of the environmental factors — UV-radiation, moisture, and biological factors of the soil. The possibility to initiate degradation of the polymer, as research shows, is provided by the addition of functional additives into the composition during the manufacturing process. It could be natural polymers like starch, pectin, cellulose [1–4], plasticizers [5, 6], metal-containing prooxidants [7–10].

Earlier, we have developed components of complex additives based on pectin [11], chitosan [12], carbohydrates, nitrogen-containing compounds, and natural oils [13], accelerating the polyolefin degradation. The optimal amount of functional additives of natural origin (starch, cellulose) was found to be 30–50 wt.% that significantly reduces the strength characteristics of the polymer materials [14–16].

The aim of this work is to investigate the effect of functional additives based on glycerol (Gly), soybean oil (SO), and polyvinyl alcohol (PVAL), plasticized by soybean oil (SO), and glycerol (Gly) on the degradability of polyethylene compositions.

The choice of such functional additives is aimed at reducing the degree of crystallinity of polyethylene to ensure the efficiency of destructive processes. It is known that compounds with hydroxyl groups in their structure play a significant role in reducing the degree of crystallinity. One of such compounds is polyvinyl alcohol modified with glycerine or soybean oil. A decrease in the degree of crystallinity of polyethylene due to the introduction of polyvinyl alcohol, as a degradable polymer, was investigated in [17, 18].

2. Experimental

Low density polyethylene (LDPE) with a melt flow rate (MFR) of 1.67 g/10 min was used for preparation of film samples. Binary functional additives based on PVAL ($MM = 1.035\cdot10^4$) and soybean oil (DSTU 4534:2006) or glycerol were obtained by mixing them at room temperature at a mass ratio of 9:1. The film compositions containing PE and binary functional additives based on PVAL were prepared by mixing and further pressing at a temperature of (125±1)°C. The films were tested for strength according to GOST 14236 after exposure to UV-irradiation and biological soil factors for 120 days.

UV-irradiation was carried out in a standard climate chamber at a temperature (38±2)°C and humidity (96−2) % for 120 days. The influence of biological soil factors was investigated by keeping specimens in the soil with pH 7 at (38±2)°C for 120 days.

The samples were studied by pyrolysis mass spectrometry (PMS) on a MX 1321 mass-spectrometer in the temperature range 25–400°C at a heating rate of (6±1)°C/min. Mass-spectra were processed using specially designed software which makes it possible to determine the intensity of decomposition

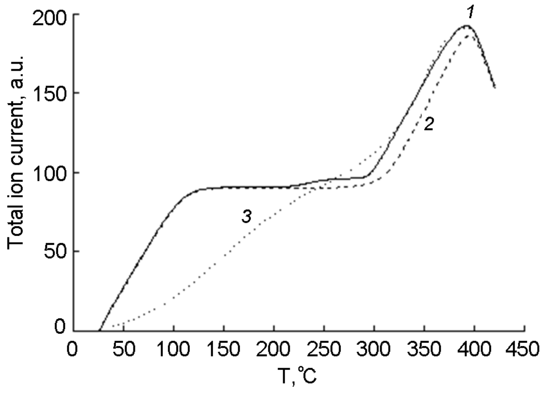

Fig. 1. The temperature dependences of total ion current of volatile products release (thermodestruction) of the neat PE (*1*), PE after UV-irradiation (*2*), and soil biological factor as well (*3*).

Table 1. The composition of PE with functional plasticizing additives and their physico-mechanical characteristics after exposure to UV-irradiation and biological soil factors

No.	Sample	Composition		Initial characteristics		After UV-irradiation		Loss after UV-radiation		After soil biological factors impact		Loss after soil biological factors Impact	
		PE	Functional additives	σ_r, MPa	ε_r, %	*sigmaБZZA* $_r$, MPa	ε_r, %	σ_r, MPa	ε_r, %	σ_r, MPa	ε_r, %	σ_r, MPa	ε_r, %
1	PE Glycerol	90	10	7.15	350.3	3.57	9.00	50.06	97.43	6.45	177.59	9.79	49.31
2	PE PVAL + glycerol	99	1	13.75	73.9	3.45	6.94	74.90	90.60	10.22	69.06	25.67	6.54
3	PE SO	95	5	11.50	693.1	3.20	8.20	72.17	98.81	8.20	58.44	28.69	91.56
4	PE PVAL + SO	95	5	8.85	34.5	0.39	10.76	95.59	68.81	8.60	40.84	2.80	18.30
5	PE	100	–	7.40	208.8	8.36	29.28	+12,97	85.97	7.69	691.60	+3.91	+231.2

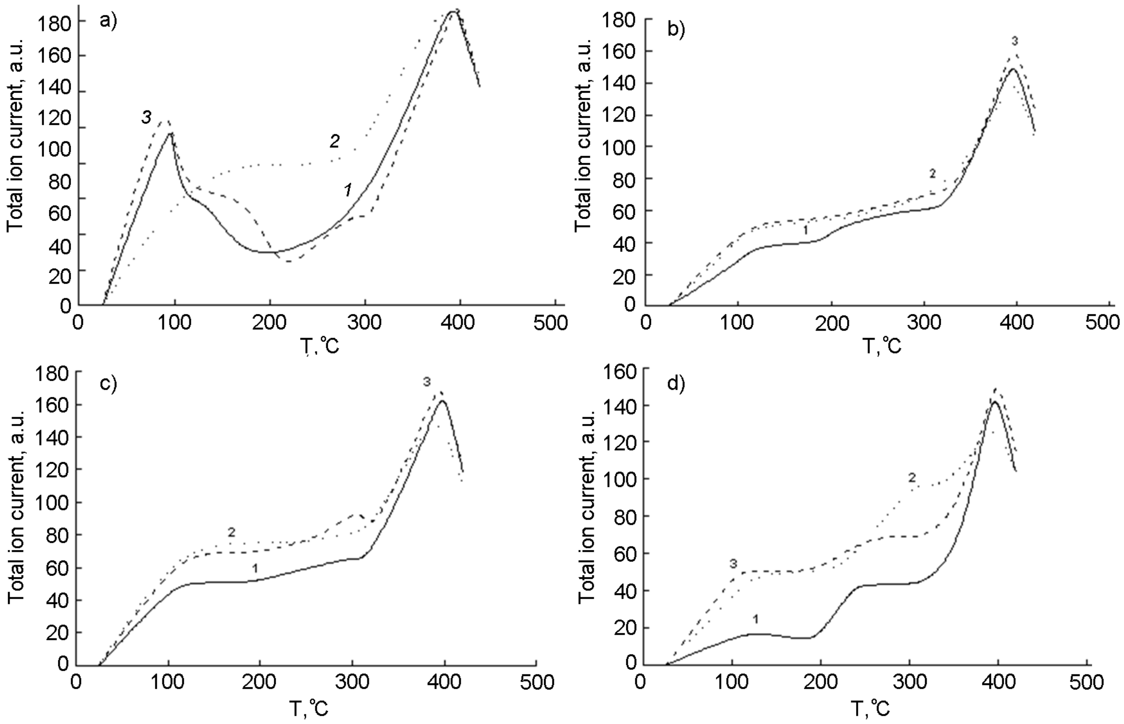

Fig.2. The dependences of total ion current of volatile products release from the temperature for PE samples No.1–4 with functional additives: initial (*1*), after UV-radiation (*2*), and soil biological factor (*3*).

of each volatile product by the area under the corresponding peak.

The temperature dependences of changes in the release of volatile products (total ionic current (I) in relative units), the intensity of thermal destruction of the samples under study, the composition of ionic fragments at different temperatures, and their individual specific intensity determined in arbitrary units, have been investigated.

3. Results and discussion

Table 1 shows the composition of PE with glycerol, soybean oil, and modified PVAL as functional additives and their physico-mechanical characteristics — strength (σ_r) and elongation (ε_r) after the action of UV-irradiation and biological soil factors. According to the above data (Table 1), the strength of the pure PE (sample 5)

Table 2. Indicators of thermal degradation in the pyrolysis of PE with functional additives at the maximum

Sample number	Initial			After UV irradiation			After biological soil factors		
	I, rel.units	*K*, n	max *m/z*	*I*, rel.u.	*K*, n	max *m/z*	*I*, rel.u.	*K*, n	max *m/z*
1	165	32	126	165	43	126	166	24	111
2	149	76	210	138	70	196	156	80	252
3	155	48	169	146	33	125	168	55	169
4	146	81	238	127	54	154	157	82	252
5	165	45	140	165	44	139	160	42	154

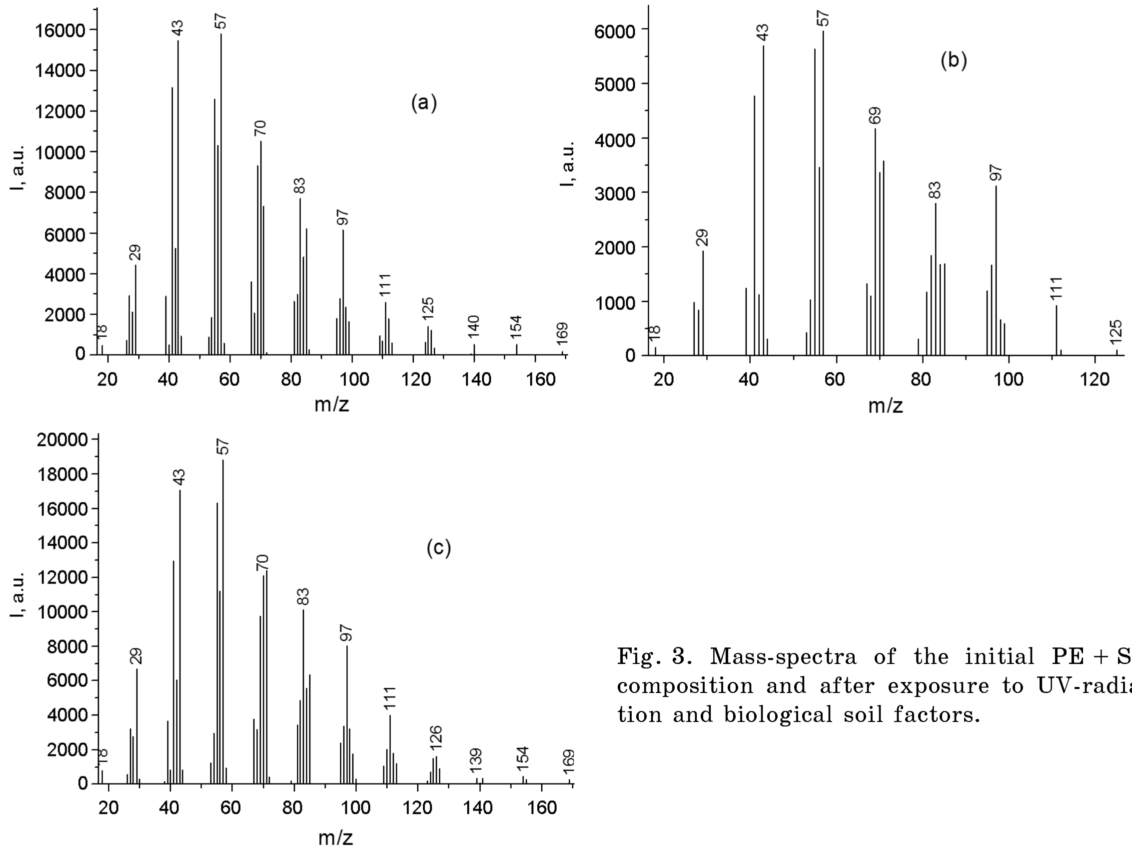

Fig. 3. Mass-spectra of the initial PE + SO composition and after exposure to UV-radiation and biological soil factors.

after exposure to destructive factors of both UV irradiation and biological factors of the soil increases.

That is, the effective biodegradation of PE without additives during ageing does not likely occur. It is important to note that the initial tensile strength increases for all compositions except for the first (PE-Gly) and the highest value was obtained for the sample containing simultaneously PVAL and glycerol. An increase in elongation (ε_r) is observed for the samples with SO or Gly as the plasticizing additives (samples 1 and 3). The most significant changes in physical-mechanical characteristics of all compositions took place under UV-irradiation, resulting in a loss of strength from 50 % to 95.59 % and losses of elongation from 69 % to 99 %. The action of biological factors of the soil did not lead to similar changes. The most significant losses were found for the sample plasticized by SO (sample 3) — 28.69 % and 91.56 % for tensile strength and elongation, respectively.

The above data exhibit that the plasticization of PE by adding of SO (sample 3) and PVAL modified with SO and glycerol (samples 2 and 4) is effective and provides losses of physical and mechanical characteristics under UV-irradiation and biological soil factors.

Mass-spectrometric studies of the samples were aimed at determining the struc-

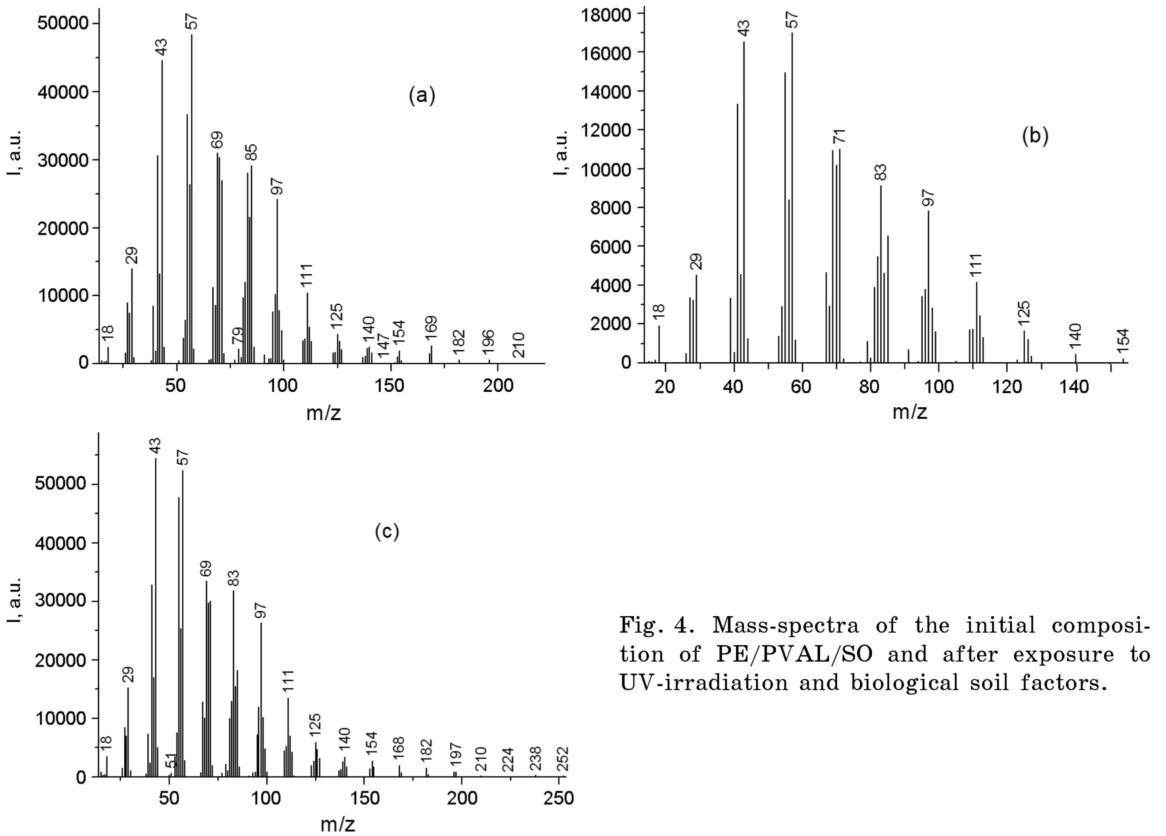

Fig. 4. Mass-spectra of the initial composition of PE/PVAL/SO and after exposure to UV-irradiation and biological soil factors.

tural changes in the PE compositions with functional additives that accelerate degradability, which were identified during physical and mechanical tests.

The mass-spectrometer allows the determination of ion fragments in the range of mass numbers 1–4000. Fig. 1 shows the temperature dependences of the total ionic current as a result of the release of volatile products (during thermal destruction) for pure samples of PE and PE exposed to biological factors of the soil and UV irradiation.

The results of mass-spectrometric investigation of PE samples with functional additives are depicted in Fig. 2 (a, b, c, d). The figure shows that the intensity of the release of volatile products after exposure to destructive factors increases in comparison with the initial sample at lower pyrolysis temperature, which would be additional evidence of a structural change in the composition due to the introduction of functional additives.

Table 2 shows the characteristics of thermal destruction of PE with the maximum amount of functional additives: the intensity of the ion current (I), the number of ion fragments (K), and the maximum molecular weight of the fragment (max m/z). The above data indicate that UV radiation most significantly affects the degradation of sample properties: a decrease in the number of ionic fragments and the maximum m/z in the compositions of samples 2, 3, 4; this is confirmed by their physical and mechanical characteristics. Fig. 3 and 4 represent the mass-spectra of the PE plasticized with SO and PVAL + SO; it can be seen that the intensity and composition of volatile products decrease after exposure to destructive factors.

Table 3 shows the changes in the specific intensity of characteristic ion fragments of PE samples with the functional additives — SO (sample 3) and PVAL + SO (sample 4). The results indicate that the greatest decrease in the intensity of ionic fragments occurs after UV-irradiation, apparently due to the fact that partial destruction of the compositions occurred under the influence of UV light.

Thus, it can be stated that the plasticization of PE by soybean oil, as well as by PVAL, modified by glycerol and SO in concentrations of 1–5 wt. %, causes structural transformations in the PE compositions and initiates destructive processes under the action of UV-radiation and biological factors.

4. Conclusions

The degradability of polyethylene with the addition of polyvinyl alcohol modified with plasticizing additives of glycerin or soybean oil has been investigated. It was found that the addition of soybean oil and

Table 3. Changes of specific intensity of characteristic ionic fragments for the samples No. 3 and No. 4 after their exposure to UV-radiation and biological soil factors

m/z	Ion fragment	Sample 3			Sample 4		
		$I{\cdot}10^4$ rel.u./ΔI, %			$I{\cdot}10^4$ rel.u./ΔI, %		
		Initial at T = 390°C	After UV at T = 389°C	After soil at T = 390°C	Initial at T = 390°C	After UV at T = 389°C	After soil at T = 390°C
57	C_4H_9	1.58	0.59/62,6	1.88/+18.9	4.84	1,69/65.0	5.24/+8.26
43	C_3H_7	1.54	0.57/62.9	1.70/+10.4	4.46	1.65/63.0	5.45/+22.0
41	C_3H_5; C_2HO	1.31	0.48/63.3	1.29/1.52	3.06	1.33/56.5	3.28/+7.2
55	C_4H_7; C_3H_3O	1.25	0.56/55.2	1.63/+30.4	3.67	1.49/59.4	4.77/+29.9
70	C_5H_{10}	1.05	0.33/68.6	1.21/+15.2	3.03	1.02/66.3	2.97/1.98
56	C_4H_8	1.03	0.35/66.0	1.12/+8.7	2.64	0.84/68.2	2.54/3.78
69	C_5H_9; C_3H_5CO	0.93	0.42/54.8	0.97/+4.3	3.10	1.09/64.8	3.35/+8.06
83	C_6H_{11}	0.77	0.28/63.6	1.01/+31.2	2.80	0.91/67.5	3.18/+13.5
71	C_5H_{11}; C_3H_7CO	0.73	0.36/50.7	1.24/+69.8	2.70	1.10/59.2	3.01/+11.5
85	C_6H_{13}; C_4H_9CO	0.62	0.17/72.6	0.63/+1.6	2.91	0.65/77.6	1.82/37.4
97	C_6H_9O; C_7H_{13}	0.61	0.31/49.2	0.80/+31.1	2.42	0.78/67.7	2.63/+8.7
42	C_3H_6; C_2H_2O	0.52	0.11/78.8	0.61/+17.3	1.31	0.09/93.1	1.70/+29.7
84	C_6H_{12}; C_4H_8CO	0.48	0.17/64.6	0.55/+14.6	2.16	0.46/78.7	1.55/28.2
29	CHO; C_2H_5	0.44	0.19/56.8	0.67/+52.2	1.31	0.21/83.9	1.53/+16.8
Total number of fragments in area m/z		48	33	55	81	54	82
Max m/z		169 $C_{11}H_5O_2$ $C_{12}H_{25}$	125 $C_7H_9O_2$ C_9H_{17}	169 $C_{11}H_5O_2$ $C_{12}H_{25}$	238 $C_{16}H_{14}O_2$	154 $C_9H_{14}O_2$	252 $C_{15}H_{24}O_3$

binary functional additives based on polyvinyl alcohol modified with soybean oil or glycerol to polyethylene leads to an increase in the initial strength of the composition in comparison with the initial PE; at the same time, after exposure to UV radiation and biological factors of the soil, the strength significantly decreased due to destructive processes. Mass spectrometric study of the sample composition showed that due to functional additives containing soybean oil, glycerol, and PVAL, structural changes occurring in PE, accelerate degradability under the influence of destructive factors.

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