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Mechanical characteristics of polyethylene

Механические характеристики полиэтилена

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Abstract. An experimental data about the effect of long-term natural aging without load and aging of samples under tensile stress on the mechanical characteristics of low density polyethylene (LDPE) under uniaxial tension are presented. A comparison between the mechanical characteristics of unstabilized and stabilized by a 2 % soot content of polyethylene is made. The influence of long-term impact of ash on the strength of polyethylene is estimated. The dependences for calculating the resource of the impervious elements of structures are given. It is shown that low density polyethylene composites have higher mechanical characteristics than the main component. It is substantiated that polyvinylchloride, manufactured using thirty percent of technological and forty percent of operational PVC waste, has high and stable mechanical characteristics. The influence of long-term aging and the effect of environments have been estimated. It is determined that the glass-filled polyamide and polyamide containing from twenty five to seventy percent of the technological waste has sufficient structural strength.

Аннотация. Представлены экспериментальные данные по влиянию многолетнего естественного старения без нагрузки и старения образцов под растягивающей нагрузкой на механические характеристики полиэтилена низкой плотности (ПЭНП) при одноосном растяжении. Дано сравнение механических характеристик нестабилизированного и стабилизированного двухпроцентным содержанием сажи полиэтилена. Оценено влияние долговременного воздействия золы на прочность полиэтилена. Приведены зависимости для расчета ресурса противофильтрационных элементов конструкций. Показано, что композиционные материалы на основе полиэтилена низкой плотности имеют более высокие механические характеристики, чем основной компонент. Обосновано то, что поливинилхлорид, изготовленный с использованием тридцати процентов технологических и сорока процентов эксплуатационных отходов поливинилхлорида, имеет высокие и стабильные механические характеристики. Оценено влияние многолетнего старения и воздействия сред. Определено, то, что стеклонаполненный полиамид и полиамид, содержащий от двадцати пяти до семидесяти процентов технологических отходов, обладает достаточной конструкционной прочностью.

Introduction

Structure protection against groundwater and surface water (spring waters, precipitation and flood) is a topical branch in hydrotechnical, road, industrial and civil engineering. In the process of sumps, waste collectors, heaps and pool converters operation there is a danger of a leakage of ecologically unsafe substances, which differ from each other in composition and the degree of aggressiveness. Natural and artificial ponds rise the groundwater on adjoining territories, which prevents the economical activity of people. Impervious structures are used for ground and soil structures protection. Different ways of installation of impervious structure elements in soil, foundations, slopes, weirs and dams are known. Laying of the polymer panels on the slopes of the soil structures under the layer of the bulk material, trench and trenchless (vibratory) screen drives are applied. Polymer impervious screens, curtains and membranes are widely spread. Most of the film members were made and are made of low-density polyethylene (LDPE), but other polymer and composite polymer materials are becoming more and more popular.

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There is a wide range of research material about designing problems of impervious hydrotechnical structures [1–4], creation and application of new waterproofing materials [5–8], polymer film screen study and construction [9–12]. The names of E.N. Bellendir, A.L. Goldin, Vatin N.I., V.G. Glagovsky, B.M. Davidenko, V.D. Glebov, V.P. Lysenko, A.I. Belyshev, S.P. Paremud, E.S. Argap, S.N. Starshinov and etc. are quiet famous in this field. It is obligatory to check corrosion and durability resistances of polymer and composite materials of impervious structures, used in active and aggressive environment [13]. The questions of application of polymer and composite materials, made with the use of technological and operational waste, in impervious structures are topical today [14–16]. Almost all materials have variable properties in time (ageing), especially polymer and composite polymer materials [17, 18] and others, for example, steels and alloys [19]. The speed of ageing depends on the sensitiveness of the material to the applied factors and their intensity. The changes of the material properties can be reversible and irreversible. The reversible ones are disappearing almost completely after the removal of stimulant exterior factors. The opposite situation takes place in irreversible changes. As we aim to predict the durability of ready-made materials, so we can define ageing as appearance of transformation during storage and exploitation.

The objectives of the present paper are:

1. To estimate the impact of the long-term ageing under load on the mechanical characteristics of the LDPE samples.
2. To compare the results of the experiment with LDPE samples stabilized with 2% soot content under long-term ageing conditions and under influence of CHP ash.
3. To compare the mechanical characteristics of LDPE samples and of LDPE samples stabilized with soot content.
4. To provide the calculation dependences of impervious elements resource considering long-term durability of the material.
5. To provide data about mechanical characteristics of the materials, perspective for applying in impervious structures.

The estimation of the influence of the long-term ageing on mechanical characteristics of low-density polyethylene during storage and under load

The samples and equipment

LDPE samples were made in laboratory complex in All-Union Scientific Research Institute of Hydraulic Engineering named after B.E. Vedeneev. The samples had a shape of a shoulder blade with 25 mm working part length and 3.5 mm width. The thickness was ranged from 0.048…0.064 mm to 0.16…0.23 mm.

Samples of stabilized LDPE had a shape of a shoulder blade with 30 mm working part length, 3.5 mm width and thickness $\delta = 0.58 \ldots 0.65$ mm.

LDPE and stabilized LDPE samples were cut in the direction and cross-direction of the film extrusion.

Uniaxial sample tension tests were carried out using FPZ-100/1 and RMI-5 (РМИ-5) installations with different capture displacement speeds (v, mm/min.). Depending on the thickness, the samples were grouped in three, then were tested and results of the experiment were presented as the mean values. The experiments with long-term loaded samples were held on one specimen. The dimensions of these samples were determined before tension test.

The results of tests

Mechanical characteristics ($\sigma_{\rho r}$– proportional limit, σ_ρ и ε_ρ – limit stress and deformation, E_ρ – elastic modulus) of low-density polyethylene (LDPE) under tension (v = 50 mm/min., $\delta = 0.16 \ldots 0.23$ mm) are shown in Table 1.

Table 1. Mechanical characteristics of LDPE in original state (the mean values of 3 samples)

Group of samples	In the direction of the film extrusion				In the cross-direction of the film extrusion			
	σ_{pr}, mPa	σ_{p}, mPa	ε_{p}, %	E_{p}, mPa	σ_{pr}, mPa	σ_{p}, mPa	ε_{p}, %	E_{p}, mPa
1	8.70	15.30	450	73.2	8.44	13.64	470	149.8
2	8.98	16.87	460	154.0	8.39	16.48	540	79.8
3	9.02	16.78	472	110.8	8.73	15.89	512	89.2
4	8.29	15.79	445	105.9	8.36	15.40	558	92.6
5	8.81	16.87	450	109.4	8.68	9.37	295	84.8
Mean	8.76	16.32	455	110.7	8.52	14.16	475	92.2

LDPE samples (in the direction of the film extrusion) have more stable mechanical properties and higher density than samples, made crosswise of the film extrusion.

Limit stress and the value of the elastic modulus are higher in samples cut in the direction of the film extrusion, than in samples cut in the cross-direction of the film extrusion. The influence of the sample thickness in specified range on LDPE mechanical characteristics (Table 1) is insignificant. The results of tension tests (v = 50 mm/min.) of LDPE samples (along of the extrusion) with thicknesses δ = 0.048…0.064 mm confirm this conclusion (Table 2).

Table 2. Mechanical characteristics (in the direction of the extrusion) of LDPE samples

Sample №	δ, mm	σ_{pr},mPa	σ_{p}, mPa	ε_{p}, %
1	0.052	7.19	14.32	275
2	0.051	8.13	13.93	240
3	0.054	8.59	16.97	360
4	0.064	7.55	16.09	395
5	0.048	8.47	15.40	295
Mean	0.054	7.98	15.34	317

LDPE samples (δ = 0.16…0.23 mm) were loaded by constant tensile load during 189–194 months (~16 years). In the first series of experiments (189 months), initial stresses of ageing under load σ_H were recorded. In the second series of experiments (194 months), beside σ_H, the relative deformation of LDPE samples was recorded in the beginning (ε_H) and in the end ($\varepsilon_к$) of ageing. Tables 3–5 show the results of experiments (σ_{ut} – the durability limit under tension, ε_{nt} – deformations corresponding to the durability limit). Table 6 shows the data of the comparison of obtained results.

Table 3. Mechanical characteristics of LDPE (in the direction of the extrusion) after long-term (189 months) uniaxial compressive loading

Sample №	σ_H, mPa	σ_{pr}, mPa	σ_{p}, mPa	ε_{p}, %	E_{p}, mPa
1	0.87	2.93	10.55	336	132
2	1.31	5.77	16.16	503	138
3	1.76	5.77	14.01	470	137
4	2.18	5.84	12.59	298	142
5	2.63	5.49	13.86	483	133
Mean	-	5.17	13.43	418	136

Table 4. Mechanical characteristics of LDPE (in the direction of the extrusion) after long-term (194 months) uniaxial tensile loading

Sample №	σ_H, mPa	ε_H, %	ε_κ, %	σ_{pr}, mPa	σ_ρ, mPa	ε_ρ, %	E_ρ, mPa	σ_{ut}, mPa	ε_{ut}, %
1	2.63	5.3	6.3	5.50	13.86	480	135	13.86	+
2	5.36	20.8	26.9	5.52	13.63	146	125	13.46	47.0
3	6.25	38.5	59.2	4.71	14.69	78	126	15.25	46.2
4	7.15	51.7	71.2	4.96	17.08	140	122	17.48	41.9
5	8.03	94.5	118.9	5.60	25.21	131	123	25.21	41.8
Mean	-	-	-	5.26	16.89	195	126	17.05	44.2

Table 5. Mechanical characteristics of LDPE (in the cross-direction of the extrusion) after long-term (194 months) uniaxial tensile loading

Sample №	σ_H, mPa	ε_κ, %	σ_{pr}, mPa	σ_ρ, mPa	ε_ρ, %	E_ρ, mPa	σ_{ut}, mPa	ε_{ut}, %
1	0.85	2.4	4.96	12.80	707	85	8.41	27.3
2	2.56	5.6	4.54	12.20	572	80	8.65	-
3	4.26	10.0	4.56	10.88	480	72	-	-
4	5.11	24.4	3.75	14.69	540	58	10.31	57.8
5	5.95	21.2	4.04	17.69	487	95	12.69	42.5
6	5.95	30.4	3.96	12.07	224	65	12.24	52.1
Mean	-	-	4.30	13.39	502	81	10.46	44.9

Table 6. Mean values of LDPE mechanical characteristics in original state and after long-term ageing under the load

The sample direction	The sample state	σ_{pr}, mPa	σ_ρ, mPa	ε_ρ, %	E_ρ, mPa
Direction of the extrusion	Original	8.76	16.32	455	111
	Original (thin samples)	7.98	15.34	317	-
	After loading 189 months	5.17	13.43	418	136
	After loading 194 months	5.29	16.89	195	126
	After loading σ_H< 3 mPa	5.22	13.50	428	136
	After loading σ_H> 3 mPa	5.20	17.65	124	124
Cross-direction of the extrusion	Original	8.52	14.16	475	92
	After loading 194 months	4.30	13.39	502	81
	After loading σ_H< 3 mPa	4.75	12.50	640	82
	After loading σ_H> 3 mPa	4.08	13.83	433	80

Let us consider the results of the LDPE stabilized by 2% content of soot tests. Samples of the first series were kept in conditions of heated (without sunlight access) warehouse space during 17 years, and the samples of the second series – in the ash of Magadan CHP during the same time. The samples are oriented in the cross-direction of the extrusion. In each series of the tests, 3 samples were used. Table 7 shows results of the uniaxial tension tests and Table 8 shows their comparisons.

Table 7. Mechanical characteristics of stabilized LDPE samples

Series №	V, mm/min.	I series				II series			
		σ_{pr}, mPa	σ_{nt}, mPa	ε_{nt}, %	E_ρ, mPa	σ_{pr}, mPa	σ_{ut}, mPa	ε_{ut}, %	E_ρ, mPa
1	0.4	2.5	8.7	20.3	140	6.4	9.5	20.0	100
2	2.0	3.0	10.0	20.3	180	7.0	10.7	20.8	120
3	20.0	3.5	11.4	18.0	200	7.7	12.1	19.2	135
4	100.0	4.0	12.4	18.0	240	8.5	13.2	12.5	185

Table 8. Comparison (in %) between the values of the LDPE mechanical characteristics of the second series and the first one

Mechanical characteristics	The deformation speed V (mm/min.)			
	0.4	2.0	20.0	100.0
σ_{pr}	+156.0	+133.0	+120.0	+112.0
σ_{nt}	-9.2	+7.0	+6.1	+6.4
ε_{nt}	+1.5	+2.5	+6.7	-30.6
E_ρ	-28.6	-33.3	-32.5	-22.9

Table 9 shows the results of uniaxial tension tests of LDPE samples (stabilized with 2% soot content) in original state (I) and after ageing (II) during 18 years. The deformation speed was 50 mm/min.

Table 9. Mechanical characteristics of stabilized LDPE in original state and after 18 years of ageing in natural storage conditions

The direction of the sample cutting	σ_ρ, mPa		Change, %	ε_ρ, %		Change, %
	I	II		I	II	
In the direction of the extrusion	14.9	16.8	+ 12.8	476	633	+ 33
In the cross-direction of the extrusion	12.9	11.8	- 8.5	552	575	+ 4.2

Conclusions on the first part of article

1. LDPE samples cut in the direction of the film extrusion in original state have more stable mechanical properties and higher values of limit stresses (on 13 %) and elastic modulus (on 17%), than samples oriented in the cross-direction of the extrusion. That was pointed in papers of other authors.
2. The influence of the sample (film) thicknesses ranged 0.043…0.23 mm on LDPE mechanical characteristics is almost insignificant (considering the dispersion of the results of the experiments), excluding the limit deformations, which are lower in thin films (0.048–0.056 mm) on 30%, than in films with 0.16…0.23 mm thicknesses.
3. Long-term ageing of LDPE samples under load (16–17 years) decreases the proportional limit σ_{pr} on 40 % (in the direction of the extrusion) and the values of the elastic modulus are

changing in different directions, i.e. increasing on 22 % (in the direction of the extrusion) and decreasing on 12 % (in the cross-direction of the extrusion).

4. The ageing of LDPE samples under load with stresses less than 3 mPa decreases the limit stresses σ_{pr} on 17 % (in the direction of the extrusion) and on 12 % (in the cross-direction of the extrusion). With long-term LDPE prestresses higher than 3 mPa the increasing of the tensile limit stresses on 8 % (in the direction of the extrusion) with decreasing the limit deformations more than triple is marked. With the increase of long-term stresses $\sigma_{н}$ the increase of the limit stress $\sigma_{pн}$, the density limit σ_{nt} under subsequent uniaxial tensile loading is marked.
5. The mechanical characteristics of unstabilized and stabilized by 2 % soot content LDPE are insignificantly different. There is an influence on durability limit σ_{ut}, elastic modulus E and proportional limit σ_{pr} of the deformation speed.
6. The influence of the ash from Magadan CHP during 17 years does not change catastrophically the stabilized LDPE mechanical properties. The proportional limit increases more than on 110 % and the elastic modulus decreases on 29 % (average) in comparison with the same characteristics of samples kept in conditions of heated warehouse space during the same time. The limit stresses and deformations were changing insignificantly. The valuable changing of the elastic modulus under stretching has to be considered in calculations of film impervious structures, because the elastic modulus E is a parameter of calculating dependences [2, 9, 11, 12].
7. The natural ageing during 18 years of stabilized LDPE does not lead to significant changes of limit stresses and deformations.

The long-term durability of the film polymer materials and the calculations of the impervious structure resource

Let us consider the durability of the polymer film impervious structures as the limit term of their functioning in structure construction in determined exploitation conditions. The durability of the polymer element is determined by exploitation loads and temperatures, technological influences, ageing of the polymer material and the matrix of composite materials.

The base for predicting the durability (resource) of the polymer structure elements is an experimental data of long-term durability of the used materials. The curves of LDPE long-term durability are represented as correlation dependences $\sigma_i = A - Blg\tau$ (σ_i – the stress intensity, mPa; τ – time, sec.). The experimental data from work [2] was used in static processing. The LDPE membranes with the diameters 6–10 mm and 80–114 mm, thicknesses 0.1 mm and 0.04 mm were tested. The first dependence $\sigma_i = 10.46 - 0.547 lg\tau$ was obtained as a result of the tests of membrane samples made of the film received from manufacturing plant. Considering the results of the short-term uniaxial tension tests, the long-term durability equation was obtained in the following form: $\sigma_i = 12.02 - 1.064\ lg\tau$. The results of static processing of other tests are shown in [9].

For calculating film elements for design scheme of membrane under hydrostatic pressure, the following depending was obtained:

$$\frac{3.8}{S_{adm}} = \int_D^\tau \left[\sqrt[3]{E(\tau)\left(\frac{\alpha_э d_ф}{\delta}\right)^2 q^2(\tau)}\right] \cdot \left[\frac{0.434B}{\xi(A - Blg\xi)^2}\right] d\theta,$$

where: S_{adm} – a safety factor for damages;

$E(\tau)$ – an elastic modulus (mPa) of the material depend on the exploitation time;

$\alpha_э$ – an efficiency factor of pore radius, which value depend on soil fraction [2];

$d_ф$ – a minimal size of the cushion soil fracture;

δ – a film thickness when a homogeneity factor is $k_{ogn} = 1$;

$q(\tau)$ – uniformly distributed load (hydrostatic pressure, mPa) changing in time in general case;

$\xi = (\tau - \theta)$ – time, sec.;

A u B – constants of the correlation equation of the long-term durability (50% probability of destruction).

In another version S_{adm} = 1, but A and B have to be selected with long-term durability curve corresponding to the little probability of material destruction. The influence of technological and exploitation impacts is considered by A and B constants.

When there is a soil settlement (Δ – a vertical settlement, *l* – a horizontal projection of a sagging part)

$$\frac{1}{S_{adm}} = \int_0^{\tau} \left[(l/\delta)q(\tau)\sqrt{(l/2\Delta)^2+1}\right]\left[\frac{0.434B}{\xi(A-Blg\xi)^2}\right]d\theta.$$

In an article [20] the calculated dependences $q - lg\tau$ are compared to the results of the experiments.

Table 10 shows the results of the durability calculations of the film impervious elements by the first suggested dependence.

Table 10. The design durability of LDPE film impervious elements ($d_Ф$ = 12 mm)

E, mPa	**Durability ($\tau_{расч}$), year**					
	Hydrostatic pressure 50 m			Hydrostatic pressure 100 m		
	δ, mm	S_{adm}		δ, mm	S_{adm}	
		1,0	1,25		1,0	1,25
150	1.56	47.6	33.0	6.67	39.4	24.8
100	1.26	47.4	31.3	9.16	58.6	40.7
50	0.91	48.1	31.8	10.00	94.6	74.1
150	0.55	8.9	3.8	2.77	9.1	3.9
100	0.45	9.0	3.9	2.26	9.1	3.9
50	0.37	12.3	5.8	1.60	31.7	18.9
150	0.30	1.7	0.4	1.51	1.7	0.5
100	0.25	1.8	0.5	1.24	1.7	0.5
50	0.17	0.4	0.1	0.87	1.1	0.4

In calculations the values of the film impervious membrane thicknesses (δ) ($\alpha_э = 0{,}55$) were taken from thesis [2]. The probability of the film impervious membrane destruction during designed exploitation period with S_{adm} = 1.25 is not higher than 5 %.

The information about the mechanical characteristics of materials promising for using in impervious structures

The mechanical characteristics of polyethylene of high density and composite material on its base with polyethylene of low density

The main component of composite material is HDPE marked 277 and 276. Another main component is LDPE marked 153.

The compositions (PC-1 and PC-2) include stabilizers; phosphates; benzene OA; antiseptic alkilsulfanat E-30; pigments. The polymer HDPE-276 and PC-2 (obtained by extrusion) are differ from HDPE-277 and PC-1 (obtained by casting); they have greater molar mass and polydispersity (M_n – an average numerical value of the molar mass, M_w– an average weight value of the molar mass, M_w/M_n).

The uniaxial tension tests of plane samples (type 2 Russian State Standard GOST 11262-80) in short-time loading conditions (V=5mm/min.) and cyclic bending tests (f = 5 Hz) are carried out using XP-08 installation in the laboratory of physical and mechanical tests of plastics NGO "Plastpolymer". The fatigue tests in uniaxial tension conditions in the laboratory of material resistance of Peter the Great Saint-Petersburg Polytechnic University (frequency f = 5.7 Hz, asymmetrical cycle factor R = $\sigma_{min}/\sigma_{max}$ = 0.5). The experiments were held under nominal stresses by maintaining determined value of the maximal tensile force by cycle. The longitudinal strain was measured on a base of 20 mm with the help of an optical cathetometer.

Table 11 shows the results of polymer and polymer composite materials tests (σ_{nt} – the destruction limit, σ_y – the yield strength, ε_p – the limit deformation, N_{cp} – an average number of cycles before sample destruction under bending, ε_p^{max}– the limit deformation under cyclic uniaxial tension). The fatigue curves $\sigma_{max} = C - Д lgN$ under tension were obtained by processing the experimental data by the method of the least squares.

Table 11. Molecular characteristics and the results of polyethylene of high density and composite materials experiments

Material	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	$\frac{M_w}{M_n}$	σ_{nt}, mPa	σ_y, mPa	ε_p,%	C, mPa	Д,mPa	ε_p^{max},%	N_{cp}
HDPE-277	9	75	8.3	30.2	18.9	88	33.6	4.6	32-57	1370
HDPE-276	11	130	11.8	37.1	29.7	45	40.5	5.4	16-35	9290
PC-1	10	95	7.6	33.0	27.8	128	32.6	3.6	105-262	5797
PC-2	13	125	9.6	40.0	39.6	36	45.7	6.0	29-61	18687

Composite materials PC-1 and PC-2 have higher mechanical characteristics than the polyethylene of high density.

The usage of these composite materials in impervious structures depends on technology abilities of their obtaining on the stacking area.

The mechanical characteristics of PVC sheet fabricated with the use of technological and exploitation waste

The effective way of using all types of industrial and domestic waste, particularly polymeric waste, is their secondary recycling, which allows saving the scarce raw materials with payback costs on producing secondary materials and new composite materials with secondary material components. The prospects of using secondary materials in impervious structures are defined by their relatively low costs.

The modifications of PVS sheet were made by thermal plasticization method [21]. The basis of the new obtained materials containing from 64 % to 78 % of waste was the resin PVC-C635M (Russian State Standard GOST 14332-78). The main compositions are shown in article [21].

The mechanical characteristics of PVC fabricated with the use of technological (30 %) and exploitation (40 %) waste under short-term loadings are shown in paper [21]. From the results of the study it can be concluded, that the obtained modifications of PVC with the use of huge amount of waste have quite high and stable mechanical properties. PVC sheets have an isotropism of mechanical properties in a plane sheet.

In article [22] there are experiments of environment impact (liquid evaporating nitrogen, running water, aqueous solution of 3 % NaCl, machine oil) and natural ageing with and without an environmental impact on mechanical characteristics of the secondary PVC under linear tension. It can be concluded that PVC obtained with the use of 30 % technological and 40 % exploitation PVC waste is resistant to the impact of those environments and to the natural ageing processes.

Short-term loading tests under different deformation speeds [21] allow estimating the range of PVC deformation limits. Relatively small values of these deformations (up to 6 %) allow making tests on the long-term durability with supports and with predetermined values of conditional stresses. During long-term durability tests of one PVC modification was used the batch of identical samples from 4 to 21. Small batch of samples was used, when it was necessary to experimentally confirm really predicted result (including data from [21, 22]). The duration of tests was 10-12 days.

The experimental data was approximated by the least-squared method with the use of correlation equations of long-term durability of the form σ =A-Blg τ, where σ – measured in MPa, τ – the time of destruction, s (time can be dimensionless $\xi = \tau/\tau *$, where $\tau *$– normative time, equal to 1 s). The values of correlation equation of long-term durability factors (A and B) of PVC modifications are shown in Table 12.

Table 12. The values of correlation equation curve of long-term durability factors

PVC modifications	**The values of correlation equation curve of long-term durability factors**	
	A, MPa	B, MPa
PVC 1	56.66	3.60
PVC 4	55.66	2.66
PVC 5	56.41	3.34
PVC 8	55.31	2.42
PVC 9	58.85	3.32
PVC 10	58.24	2.59
PVC 11	57.37	3.59
PVC 12	56.06	3.01
PVC 13	58.53	3.42
PVC 14	55.88	3.03
PVC 15	61.53	3.79
PVC 16	63.34	3.53
PVC 17	64.36	4.03
PVC 18	62.01	3.69
PVC 19	52.86	3.38

Material modification samples PVC 4, PVC 15, PVC 10 and PVC 16 are made of bilayer blanks (blades). PVC 17, PVC 18 and PVC 19 samples are made of multilayered blades (while making PVC 19 sheets, less durable and with higher waste content PVC layers are used). PVC 11, PVC 12, PVC 13 and PVC 14 samples are made according to the first recipe, PVC 15 and PVC 16 are made according to the second one (in other samples the recipe is not mentioned).

The durability of bilayer PVC 5 material samples is higher, than the one of single-layered PVC 1 (both materials belong to the same batch). The same result appears while comparison between PVC 9 with PVC 10, PVC 15 and PVC 16. The discrepancy between compared PVC long-term durability curves with high stress values is not as significant as with lower stress values.

The long-term durability of PVC modifications, made according to the second recipe, is higher than the one, made according to the first recipe.

The comparison of short-tem [21] and long-term durability of PVC under uniaxial tension allows us to affirm that the high long-term durability of PVC 4, PVC 9, PVC 10 and PVC 16 correlates with the high values of short-term durability limit.

An estimation of environments (nitrogen, tap water, 3 % aqueous NaCl solution, machine oil) preliminary action on PVC modifications long-term durability is made (in [22] the influence of these environments under short-term loading on mechanical characteristics is estimated).

An influence of preliminary action of 3% aqueous NaCl solution during on tap water samples during 150 days and their subsequent one-month storage on their durability is insignificant.

Within the framework of the present work, an experimental estimation of the effect of natural aging on the storage of two-layer PVC 5 samples was conducted in room conditions and exposed to outdoor exposure without sunlight access for two years. The change in the correlation coefficients of the long-term durability can be traced from the data in Table 13.

Table 13. The correlation coefficients values of an equation of the long-term durability curve of PVC 5

The material state	The coefficients on the correlation equality	
	A, MPa	B, MPa
When delivered	56.41	3.34
After storage	57.60	2.84
After exposure	59.69	3.33

The PVC 5 long-term durability both after storage and after exposure during 2 years is increasing in comparison with the material durability in when delivered state.

The PVC 1 samples long-term durability was determined in when delivered state. The other part of PVC 1 batch at the same time was loaded with tensile loads of a predetermined value and maintained in the course of the experiment, which made it possible (about 50 %) to destroy the samples. The samples were then loaded and stored in a heated warehouse for one year. After storage, the samples were loaded again with predetermined loads until failure.

Preloading of PVC 1 samples under tension conditions a year before re-loading under the same conditions as in the case of its long-term durability, does not decreases its long-term durability and moreover, it increases $\sigma = 57.65\text{-}3.33\ lg\tau$. The explanation of this fact can be different, in particular, one can make an assumption about the effect of the workout of the material, its natural aging when stored between the series of tests. The results of the survey also show that the damages that occur during the initial loading process relaxes over time after the intermediate discharge.

PVC obtained using technological (30 %) and operational (up to 40 %) waste is characterized by high stability and long-term durability, including being in condition of preliminary action of explored environments and long-term storage, and also after preloading.

Blade elements of this material in a two-layer design have a higher tensile strength as compared to single-layer elements.

Glass fiber reinforced polyamide with the content of recycling waste for fasteners of impervious structures

In this section, data on the technology of production and the results of the conducted mechanical tests of two batches of primary glass-filled (30 % fiberglass) polyamide PA6-21OKS (OST 6-11-498-79), polyamide containing 20-75 % of recycling waste and secondary polyamide (100% recycled waste) in the state of delivery are presented. The test samples were prepared by injection molding on a thermoplastic automatic machine DE 3327-1. Mixture of primary polyamide PA6-21OKS (in granulated form) and recycled waste (gates, defective products) after crushing on a rotary-type crusher was dried to a humidity of 0.2 % in an air circulation drying cabinet at a temperature of 70-80 ℃ for 24-48 H. The main casting mode: pressure 1100-1300 kgf /cm^2. The temperature in the first zone of the cylinder was 240-250 ℃, in the second – 250–260 ℃, in the third – 260–270 ℃. The cycle time was 20–60 s. (closing of the mold form heated to a temperature of 70–80 ℃, injection of the material, holding under pressure, holding for cooling, opening the mold form, removing the product). After removing the gates, the appearance is monitored in order to detect defects and sample sizes.

The mechanical characteristics of the investigated materials under tension (Russian State Standard GOST 25601-80, σ_{ut} – strength, ε_{ut} – corresponding deformation, E_p – modulus of elasticity) were obtained from the experiments with a displacement speed of machine grippers V = 5 mm/min.

Sample bending tests (Russian State Standard GOST 25604-82) were carried out according to a three-point scheme (L = 60 mm) of loading. The following characteristics were determined: the bending strength σ_{vi}, the maximum deflection $\Delta\omega$, the elastic modulus E_u and the coefficients of variation of the average values of σ_{vi} and E_u (ϑ_σ and ϑ_E, respectively). The resilience values (a_n) and the brittleness indices σ_z were determined in a single shock bending test (Russian State Standard GOST 4647-62).

Tables 14–16 present the average values of mechanical characteristics obtained by testing three to five samples of two batches (I and II) of polyamide.

Table 14. The mechanical characteristics of PA6 – 21 OKS polyamide under tension depending of the recycle waste content

Waste content,%	σ_{ut}, MPa		ε_{ut}		*Ep,* MPa		ϑ_E, %	
	I	II	I	II	I	II	I	II
0	137.2	121.6	0.063	0.059	1750	2060	10.2	3.8
20	133.1	116.7	0.063	0.058	1880	1990	9.3	1.6
30	131.2	114.8	0.058	0.057	1930	2020	8.0	3.1
40	126.8	114.4	0.060	0.058	1930	2000	4.6	3.7
50	126.9	110.3	0.062	0.051	1860	2150	6.2	4.8
75	-	102.9	-	0.048	-	2120	-	5
100	-	98.8	-	0.045	-	2170	-	-

Table 15. The mechanical characteristics of PA6 – 21 OKS polyamide under bending depending of the recycle waste content

Waste content,%	σ_{vi}, MPa		ϑ_σ, %		$\Delta\omega$, mm		E_u, MPa		ϑ_E, %	
	I	II	I	II	I	II	I	II	I	II
0	229.3	192.9	1.2	2.2	1.10	1.12	6500	5700	2.3	8.6
20	216.2	191.1	1.7	2.0	1.23	1.12	5970	6180	4.7	0.7
30	213.4	188.4	2.7	1.9	1.19	1.19	6200	6040	2.2	1.3
40	210.4	186.5	1.3	3.1	1.25	1.19	5880	5990	1.8	0.3
50	209.2	190.7	1.9	2.2	1.27	1.22	5840	6030	4.8	3.4
75	-	189.1	-	4.7	-	1.28	-	5840	-	2.1
100	-	170.9	-	8.2	-	1.61	-	4650	-	7.6

Table 16. The mechanical characteristics of PA6 – 21 OKS polyamide under shock depending of the recycle waste content

Waste content.%	a_p. н/м		ϑ_v. %		σ_z. н/м^2		ϑ_σ. %	
	I	II	I	II	I	II	I	II
0	0.390	0.326	2.9	3.0	0.975	0.816	2.9	3.0
20	0.390	0.322	4.2	2.7	0.976	0.804	4.3	2.7
30	0.386	0.311	3.7	3.1	0.966	0.777	3.7	3.1
40	0.386	0.311	1.9	4.4	0.965	0.778	1.9	4.4
50	0.351	0.283	1.4	9.0	0.877	0.708	1.4	9.0
75	-	0.259	-	7.8	-	0.648	-	7.8
100	-	0.244	-	3.5	-	0.611	-	3.5

Based on the data presented in Tables 14-16, it can be concluded that the samples of the first batch of polyamide have higher mechanical characteristics for most of the studied parameters than in the second batch. which can be explained by some differences in the manufacturing technique. The uniform stress state produced by uniaxial stretching of polyamide samples is most dangerous in comparison with the inhomogeneous stress state arising during bending. Modulus of elasticity of polyamide PA6-21OKS with a different content of recycled waste is slightly higher (up to 5 %) than for initial polyamide and practically does not depend on the quantity of recycled wastes used for manufacturing (with the exception of data for secondary polyamide when tested for bending). Reduction of the strength characteristics of polyamide with 40 % of the recycled waste did not exceed 7 % and with a 50 % waste content – 12 % in comparison to the characteristics of the initial polyamide. Some strength characteristics of the secondary polyamide are lower on 25 % than those of the initial polyamide. It should be noted that the values of the coefficient of variation of the average values of the mechanical characteristics of the investigated modifications of PA6-21OKS for all types of tests are almost identical.

Of interest are the results of testing samples of polyamide PA6-21OKS on uniaxial compression. These samples were fabricated by mechanical treatment (rather than injection molding) from second batch samples used in tensile tests. They had the shape of a parallelepiped with dimensions 4x4x10 mm. and were laid in the grippers of plants without lubricants. The values of the mechanical characteristics (resistance. ε_{is} - deformation corresponding to this strength. E_c - modulus of elasticity) during compression of the polyamide are presented in Table 17. The displacement speed of the installation grippers was 5 mm/min.

Table 17. The mechanical characteristics of PA6 – 21 OKS polyamide (the second batch of samples) under compression depending of the recycle waste content

Waste content.%	**σ_{is} . MPa**	**ε_{is}**	**E_c. MPa**
20	100.5	0.102	2340
30	105.4	0.136	2230
40	108.0	0.146	2300
50	104.4	0.146	2330

The limit of proportionality of the polyamide under compression was equal to seventy percent of the strength limit. The modulus of elasticity of a polyamide under compression is on average 13% higher, the strength limit is 8 % smaller and the deformation under uniaxial compression is twice higher than the corresponding characteristics. The decrease in the short-term durability can be explained by the influence of the mechanical processing of the samples.

During the tests on long-term durability (static fatigue) under uniaxial compression of the second batch samples of polyamide PA6-21OKS a constant specified load and temperature (T = 20±2 ℃) were maintained. Taking into account the fact that during loading the change in the cross section of the samples did not exceed 2-3%. the processing of the results of the tests was carried out in conditional stresses. In the static least-squares treatment. the experimental data on the durability of the modification of the polyamide of the second batch were approximated by equations of the form $\sigma = A\text{-}B_{lg}\ \tau$. where σ is the tensile stress. MPa; T - time from Table 18.

Table 18. The results of processing the data of tests for the long-term strength of polyamide PA6-21OKS with a different content of recycled waste

Waste content. %	**Number of samples**		**A long-term durability equation coefficients**	
	destroyed	in the batch	A. MPa	B.MPa
0	11	11	126.6	8.0
20	8	8	124.9	8.2
30	9	9	116.4	6.6
40	9	8	114.9	6.2
50	12	9	113.0	5.9
75	8	7	120.4	6.2
100	7	5	106.9	5.2

According to the data in Table 18, it can be assumed that under high stresses and, correspondingly, short loading times, the durability of the polyamide PA6-21OKS with a different content of recycled waste varies more significantly than under low stresses (in the investigated durability range 10^6 s.), where the difference in durability is not confirmed statistically. It should be noted that several samples of polyamide with a recycled waste content of more than 40 % had a lower long-term durability than the samples in the general batch.

Experimental data on cyclic fatigue of a glass-filled polyamide with a 30 %, 40 %, and 50 % recycled waste contents are of interest. Before the tests, the samples were stored in a heated warehouse for 6 months. The loading frequency under uniaxial tension conditions was 5-7 Hz with the asymmetry coefficient of the sinusoidal cycle R = 0.5. During the experiments. the preset value of the conditioned stresses was maintained. By statistical analysis of an experimental data on the method of least squares fatigue curves were obtained: σ_{max} = C-D Lg τ. corresponding to 50 % of the probability of failure. Depending on the percentage of recycled waste in the material 30 %, 40 %, 50 %. the following values are obtained (in MPa): C_1 = 86.6. D_1 = 5.2; C_2 = 77.5. D_2 = 4.6; C_3 = 97.4 and D_3 = 9.0. The fatigue cyclic durability of polyamide PA6 -21OKS modification is below the long-term static durability.

Discussions

Today accelerated ageing is more popular way of long-term durability estimation, than natural one. However, it is impossible to estimate the accuracy of such tests without natural ageing tests. There is some experimental data, which mostly confirms the possibility to forecast the materials' behavior for 15-17 years, but no longer [5, 17]. In case of impervious structures, it is not sufficient, because they may be used for more than 50 years.

Some scientists believes it is impossible to obtain a "good imitation" by accelerated ageing, what is shown with the help of simple kinetic models in general. In any case, with this approach, the problem of the relationship between accelerated and natural aging remains unresolved. The "real approach" uses non-empirical kinetic models taking into account structural changes at all appropriate scales, and also uses the polymer physics to establish a relationship between the polymer structure and the property under consideration. An important characteristic of this approach is that accelerated aging only serves to determine the parameters of the model. [28]

Besides, the most popular test are held on materials under weather conditions with sunlight access. For impervious structures, this kind of test is useless, because the main area of implementation of such structures does not include significant sunlight and weather influences.

Thus, the issue of long-durability prediction methods is not investigated enough and seems appealing and perspective for further researches.

Conclusions

The film of the examined polyethylene of low density (LDPE) in original state has stable mechanical characteristics with some anisotropy related to the direction of the extrusion.

The LDPE long-term ageing (16-17 years) under load in heated warehouse space conditions decreases the proportional limit on 45 % (average). besides the values of the elastic modulus increases on 22 % in the direction of the film extrusion and decreases on 12 % in the cross-direction of the extrusion. The LDPE ageing under load with tensile stresses less than 3 mPa decreases limit stresses under short-term uniaxial tension up to 17 %. The LDPE ageing under load with tensile stresses higher than 3 mPa increases limit stresses under short-term uniaxial tension (in the direction of the extrusion) on 8 % with the deformation decrease more than triple. For samples cut in the cross-direction of the film extrusion, the changes are insignificant.

The mechanical characteristics of unstabilized and stabilized by 2 % soot content LDPE are insignificantly different. Natural ageing during 18 years in heated warehouse space conditions of stabilized LDPE does not lead to significant changes of limit stresses and deformations under uniaxial tension.

The influence of the Magadan CHP ash during 17 years does not change significantly the stabilized LDPE mechanical characteristics. The change of the elastic modulus (the average decrease on 29 %) has to be considered in calculations of film impervious structure elements.

The dependences for the durability (resource) calculations of film impervious LDPE structure elements and calculating resource data are shown.

Composite materials based on the HDPE of two grades and LDPE have higher mechanical characteristics than the main polyethylene component of high density (HDPE). The usage of tested composite materials has perspectives.

The polyvinylchloride fabricated with the use of technological (~30 %) and exploitation (~40 %) waste was tested under long-term and short-term loading conditions by uniaxial tension and under preliminary impact of some environments (liquid evaporating nitrogen. running water. aqueous solution of 3 % NaCl. machine oil) considering the long-term ageing before and after the environmental impact. This sheet PVC has quite high and stable characteristics. Mentioned PVC and polyamide PA6-210CS (ПА6-210КС) with the content of technological waste could be used particularly in impervious structures. In this case, the problem of the waste usage is also solved.

Finally, it is important to emphasize that today the research is continuing: now LDPE samples that have passed through natural ageing for more than 40 years are tested for strength, creep and stress relaxation.

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