

Heavy Oil Residues: Application as a Low-Cost Filler in Polymeric Materials

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Abstract

Deposits of oil sands, bitumen, extra-heavy oil, and heavy oil appear in more than 70 countries all over the world and the fraction of oil recovered gradually increases. High content of poly-condensed high molecular weight oil components (PHMOCs), which may amount up to 50-60% depending on conditions of oil formation, is the main difference of heavy oil and bitumen from conventional oil. PHMOCs can lay the foundation for the preparation of a large number of valuable materials due to their structural manifold and their potential still not discovered to full extent. This work is devoted to the study of the effect of PHMOCs on properties of the composition materials prepared from polyethylene matrix. An «asphalt» – industrial product of deasphalting of tar, as well as asphaltenes and resins isolated from heavy oil, were used as a source of PHMOCs. HDPE and fillers were characterized using MALDI, FTIR, DSC and TGA. For the new composite materials we evaluated the physicomechanical properties, the thermal decomposition characteristics (by TGA), and the accumulation rate of carbonyl groups in the oxidized polymer (on FTIR). Studies of new composite materials showed that the introduction of filler in an amount of up to 4% in a polyethylene matrix does not lead to a significant change in the physicomechanical properties, but for a number of parameters they are improved. It also figured out that the addition of PHMOCs to polyethylene makes it unnecessary to stabilize the resulting compositions with stabilizers of thermal oxidative degradation. Results of experimental studies indicate that industrial residue - «asphalt» is a promising filler and low cost of this stock renders it perfect source for the industry of polymer materials.

Keywords: HDPE; Filler; Composition; Heavy Oil; Residue; Asphaltenes; Resins; Thermo-Oxidative Destruction.

1. Introduction

Global oil reserves are 9 to 13 trillion of barrels according to International Energy Agency estimates, among which only 30% is conventional oil, while 70% corresponds to nonconventional oil (30% oil sand and bitumens, 25% extra-heavy oil, and 15% heavy oil). Deposits of oil sands, bitumens, extra-heavy oil, and heavy oil appear in more than 70 countries all over the world and the fraction of oil recovered gradually increases [1]. High content of polycondensed high molecular weight oil components (PHMOCs), which include asphaltenes and resins [2, 3], is the main difference of heavy oil and bitumen from conventional oil. Their total content may amount to 50-60% depending on the chemical nature of oils and conditions of oil formation [4]. Asphaltenes are special among oil components and represent the components with the highest molecular weight and the most complex elemental composition and molecular structure

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[5-7]. Resins possess lower molecular weight and condensation degree [8], while the alkyl chain length is higher [7]. Although the average molecular weight of resins is lower than that of asphaltenes [9], this is not a significant factor in determining the difference in the behavior of asphaltenes and resins. The main difference is associated with a lower polarity of resins' molecules [10]. As a result, asphaltenes usually defined as hydrocarbons, which are soluble in aromatic and insoluble in saturated compounds, while resins are insoluble in liquid propane and butane, but soluble in pentane and more highly molecular n-alkanes [11-14].

PHMOCs usually give deposits due to their ability to aggregate and associate [15, 16] and their high content is regarded as an adverse factor for recovery, transport, and upgrading of oil. On the contrary, PHMOCs can lay the foundation for the preparation of a large number of various valuable materials due to their structural manifold and their potential still not discovered to full extent [17-33].

Existing literature data are mainly focused on the study of asphaltenes, on the basis of which many important products are produced (including the compositions with polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), synthetic rubbers, and others), which possess higher performance characteristics than analogous industrial products. However, asphaltenes in pure form are not accessible industrial products. Residual heavy products of oil upgrading containing increased contents of PHMOCs as exemplified by tars, residues of propane-butane deasphalting of tar (asphalt), and others can be a large-scale source of PHMOCs.

Existing literature data mainly focuses on research of asphaltenes. They can be converted into carbon nanomaterials [19-21]; based on them, new composite materials with polyethylene, polypropylene, polystyrene, synthetic rubbers, etc., that have higher performance properties compared with similar industrial products [22-26] are obtained. Modified asphaltenes are widely studied. Asphaltenes modified with silane derivatives as coatings to obtain superhydrophobic nanomaterials to clean-up oil spills to be applied as an adsorbent in the large-scale removal of petroleum crude oil spills and hydrophobic organic pollutants in marine and aquatic systems [27] and as a novel reinforcing filler in epoxy resin [28]. Asphaltenes modified with styrene-ethylene-butylene-styrene (SEBS) as precursor for isotropic pitch-based carbon fiber [29]; with maleic anhydride - for the synthesis of the polystyrene-asphaltene graft copolymer, able to react chemically with paving asphalt components [30]. Asphaltenes modified with acid acquire high ion exchange and adsorption properties [17, 31-33].

However, asphaltenes in pure form are not accessible industrial products, and their modification requires additional costs. Residual heavy products of oil upgrading containing increased contents of PHMOCs as exemplified by tars, residues of solvent deasphalting (SDA) of heavy oil feedstocks can be possible large-scale source of PHMOCs for creating new polymer compositions. SDA is one of the most interesting technologies for the processing of heavy residues at modern oil refineries that requires little investment [34-36]. During the SDA process, in the presence of low molecular weight alkanes or other precipitants, in regard to which asphaltenes are lyophobic, these precipitators coagulate and entrain high molecular weight asphaltene-resinous substances in the form of solvate layers. When deasphalting is aimed at separating deasphalted oil (DAO), SDA is carried out exclusively using propane, which allows selecting the optimal amount of oil fractions of quite good quality and carrying out the process at moderate temperatures and pressures. If the target product is the residue, (PHMOCs concentrate) - «asphalt», then heavier alkanes are usually used [37].

This work is devoted to the study of the effect of oil fillers on physicochemical and other properties of the composition materials prepared from polyethylene matrix. The results obtained for the compositions on industrial residue of propane-butane deasphalting of tar, as well as asphaltenes and resins isolated from heavy oil are compared. Particular attention was devoted to the evaluation of the performance of the mentioned fillers as stabilizers of thermo-oxidative destruction.

2. Experimental Section

2.1. Materials

HDPE produced in OAO Kazan'orgsintez were used, namely, PE1 (counterpart of PE100) corresponding to the polyethylene brand for the production of pipes and PE2 brand devoted to the fabrication of household and business products. Asphalt is an industrial residue of propane-butane deasphalting of tar produced by Novoufimsk oil refinery, as well as asphaltenes and resins, which were isolated from heavy oil of Zyuzeevo deposit (Tatarstan, Russia). Composition and properties of the oil objects are given in Table 1 and elemental composition of polyethylenes and the oil objects (fillers) are given in Table 2.

Table 1. Physicochemical properties and component composition of petroleum samples

Sample	Density (at 20°C) (g/cm ³)	Viscosity (at 20°C) (mm ² /s)	Asphaltenes (wt %)	Resins (wt %)	Saturated and aromatics hydrocarbons (wt %)
asphalt	1.0762	-	13.7	40.7	45.6
oil	0.9250	472	6.9	26.9	66.2

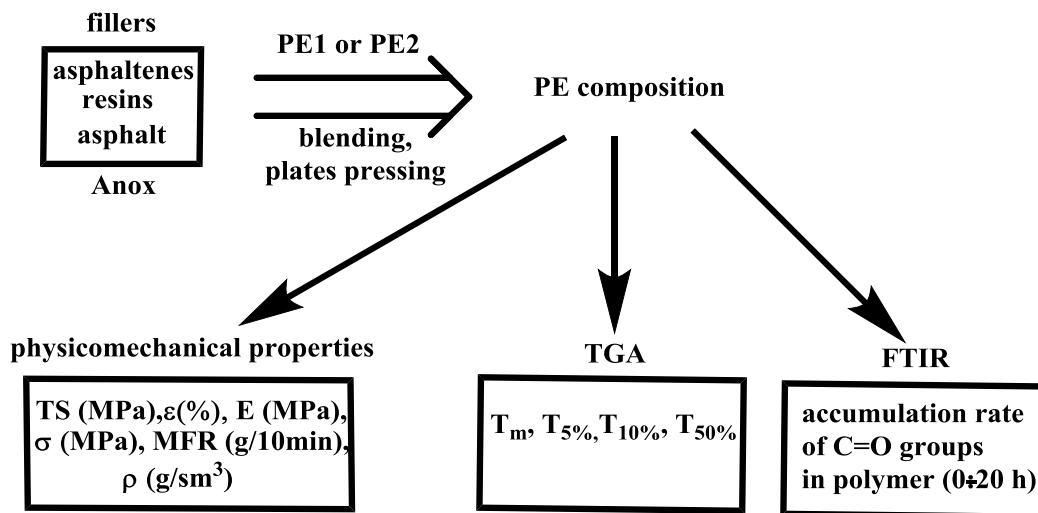
Table 2. Elemental composition of polyethylene and fillers

Sample	Content, wt %				H/C
	C	H	N	S	
PE1	84.70	15.25	-	-	-
PE2	80.52	14.96	-	-	-
asphalt	83.79	9.53	0.24	4.87	1.36
asphaltenes	79.72	8.28	1.62	10.26	1.25
resins	75.96	8.92	1.25	9.39	1.41

2.2. Methods and Equipment

Asphaltenes were precipitated from the heavy oil by 20-fold volume excess of n-hexane. After 24 h, the obtained precipitate was filtered and washed with boiling n-hexane in a Soxhlet apparatus up to decolorization of flowing solvent to remove as much maltenes as possible. The solvent from the maltene solution was removed up to a constant weight using a rotary evaporator (60 mm Hg/30⁰ C). Maltenes were separated by elution column chromatography on silica gel [38]. n-Hexane were used to elute saturated and aromatics hydrocarbons, the blend of isopropanol/benzene (1:1, v/v) - for the extraction of resins.

The polymer was mixed with filler on a Brabender mixer for 5 min at 190°C. PE specimens with asphalt, asphaltenes, resins, and Anox® 20 Powder were prepared in Figure 1. The plates that are 1 mm in thickness were prepared by pressing at the temperature of 170±5°C and exposed to pressure for 5 min.

**Figure 1. Flowchart of polyethylene compositions' research**

Tensile strength (TS), Elongation at break (ϵ), Elastic Modulus (E), and Yield strength (σ) of the compositions were determined according to ISO 527-2:2012 on an Inspect mini tensile machine. The melt flow rate (MFR) of polyethylene and its compositions was determined on an IIRT-5M plastometer at 190°C and the load of 49 N (5 kgs). Density was determined according to ASTM D792 – 13.

Elemental composition was determined using a CHNS-O Euro EA3028-HT-OM analyzer (EuroVector). Matrix-assisted laser desorption/ionization (MALDI) mass spectra were obtained by Ultra Flex III TOF/TOF mass-spectrometer (Bruker Daltonik GmbH, Bremen, Germany) in a linear mode with Nd:YAG laser ($\lambda = 266$ nm). Spectra were obtained with 25 kV of accelerating voltage and 30 ns of acceleration delay. The data were processed by using Flex Analysis 3.0 software (Bruker Daltonik GmbH, Bremen, Germany). 1, 8, 9-Trihydroxyanthracene was used as a matrix.

Infrared (IR) spectra of the compounds were recorded in the range of 4000–400 cm^{-1} on a Tensor-27 IR-Fourier spectrometer (Bruker) with the optical resolution of 4 cm^{-1} . Polyethylene specimens were prepared in the form of 1-mm plates after preliminary melting. The spectra were processed and analyzed using OPUS software (Bruker Optik GmbH).

Thermal analysis was carried out on a Q-1500D derivatograph of MOM Company (Hungary) in the temperature range of 20–1000 $^{\circ}\text{C}$ at the heating rate of oven of 10⁰ C/min. Air atmosphere in the oven is stationary. Alumina was used as inert substance. The shot of specimen was 60 mg. Melting point T_m (the temperature of minimum at corresponding section of DTA curve), stages of thermo-oxidative destruction (I–IV; the character of heat effect is also

indicated), and the temperature corresponding to the maximum weight loss T_{\max} were determined for each polyethylene specimen.

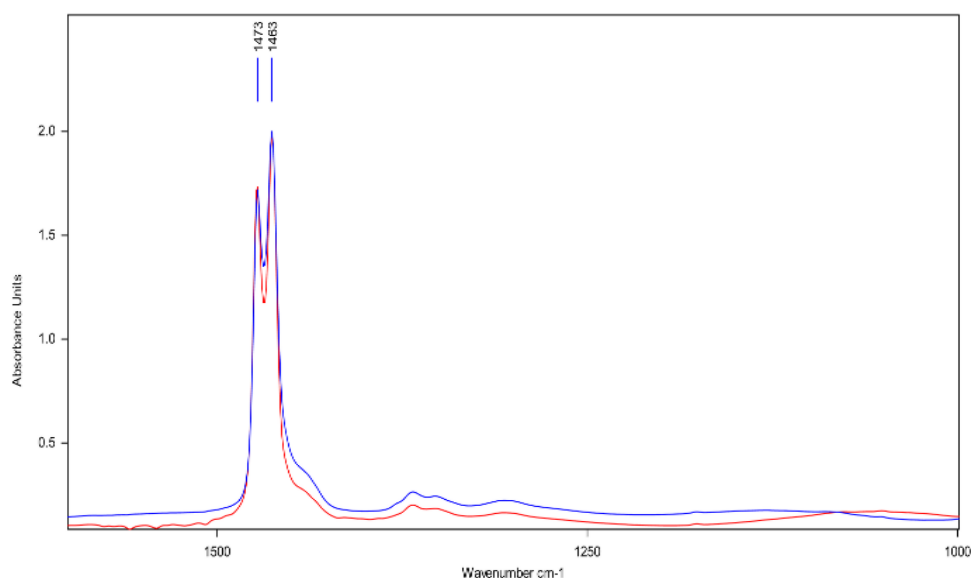
DSC curves of PE were recorded on a C80 calorimeter of SETARAM Company. Temperature scanning of a 50-mg shot was carried out in the range from 20 to 200^o C at the rate of 1^o min⁻¹. The calorimeter was calibrated by Joules effect and melting point In; the temperature measurement error was less than 0.1^oC. The melting point of the crystal phase corresponded to the temperature of minimum on the heat effect of melting. In Table 3, melting points T_m and melting enthalpy (ΔH_m) are given. The degree of crystallinity was calculated by division of the melting enthalpy of PE specimen, ΔH_m , by the melting enthalpy of PE with 100% crystallinity. It is suggested that the melting enthalpy of 100% crystalline PE is 293 J/g [24].

Performance of the fillers as stabilizers of thermo-oxidative destruction was evaluated according to TGA data (T_m and the temperature corresponding to 5, 10, and 50% weight loss of the specimen) and the accumulation rate of carbonyl groups in oxidized polymer using FTIR. The plate of the composition specimen with the size of 10 mm×10 mm×1 mm on degreased glass plate was transferred to a drying oven for thermal oxidation in the air. Thermal oxidation was carried out at 190^o C (precision of temperature maintenance is $\pm 1^o$ C) within 20 h. IR spectra were recorded before thermal oxidation after 5, 10, 15, and 20 h on a Bruker Tensor 27 FT-IR spectrometer equipped with Hyperion IR microscope (Bruker) in the range of 7500-560 cm⁻¹. The absorption band at $\nu = 1720$ cm⁻¹ corresponding to stretching vibrations of carbonyl groups of ketone and aldehyde type was used as analytical band for quantitative analysis. The bands at $\nu = 1366$ -1368 cm⁻¹ and 1305-1309 cm⁻¹, which are related to bending (wagging and twisting, respectively) vibrations of CH₃- and CH₂-groups, were chosen as internal standard. The oxidation state of polymer was evaluated according to the ratio of relative-to-integral intensities at $\nu = 1720$ cm⁻¹ and $\nu = 1366$ -1368 cm⁻¹ or 1305-1309 cm⁻¹.

3. Results and Discussion

3.1. Characterization of PE and Fillers

Determination of the intensity ratio of spectral bands I_{1368}/I_{1472} corresponding to bending vibrations of CH₂ (~1472 cm⁻¹) and CH₃ groups (~1368 cm⁻¹) is one of the variants to evaluate the quality of polyethylenes. That is, the lower the ratio, the less the number of CH₃ groups and the more homogeneous polyethylene is. In order to determine the crystal structure of polyethylene, one can use the doublet of rocking vibrations at 720 and 730 cm⁻¹, which is associated with the Davydov splitting in orthorhombic cell (the cell contains two fragments of C₂H₄). There is only one intense absorption band at 720 cm⁻¹ in triclinic crystals of polyethylene (one cell contains one fragment of C₂H₄) and in the amorphous phase [39]. In addition, these bands become narrower and better resolved with an increase in the degree of crystallinity. IR spectra of the PE specimens in Figure 2 are quite similar in the range of 720-730 cm⁻¹ and 1300-1500 cm⁻¹, which indicates identical quality of polyethylene and similar degree of crystallinity.



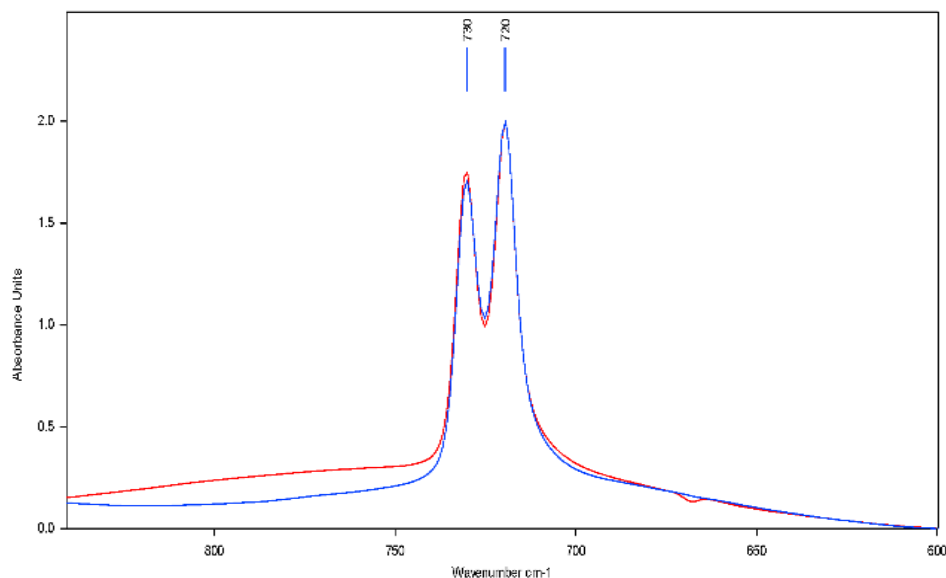


Figure 2. IR spectra of polyethylenes in the range of 1600-1000 cm^{-1} and 900-600 cm^{-1}

According to DSC data in Table 3, PE2 specimen possesses higher melting point T_m (133.7 $^{\circ}\text{C}$) and higher degree of crystallinity X_{cryst} (68.1%), which is intrinsic for linear LDP with a small quantity of short side chains. High melting point (132.9 $^{\circ}\text{C}$), as well as the medium degree of crystallinity (nearly 58%) of PE1 specimen indicates a linear character with a large number of short side chains, which restrict crystallization processes.

Table 3. DSC data of PE

Sample	T_m , $^{\circ}\text{C}$	ΔH_m , J/g	X_{cryst} , %
PE1	132.9	171.1	58.4
PE2	133.7	199.6	68.1

Several stages of destruction process can be differentiated on DTA curves of PE specimens in Table 4. Endothermic peak of melting is recorded in the temperature range of 131-133 $^{\circ}\text{C}$, which is intrinsic for LDP or HDPE. Four stages of thermo-oxidative destruction are recorded on DTA curve with a subsequent heating. I stage of decomposition of the material, which is related to its low-temperature oxidation, is caused by the elimination of low-molecular fraction in polymer, as well as the presence of weak bonds, whose cleavage initiates destruction of carbon-carbon fragments to give free radicals. Oxidizing process becomes more complicated with further heating of the specimens and exothermic (II stage) and endothermic (III stage consisting of three endotherms) effects are recorded on DTA curve. These transformations are related to deep processes of decomposition of the main chain and evolution of a wide variety of organic saturated and unsaturated volatile monomers. Complete deposition of PE occurs at stage IV (almost by 100%) with the appearance of exothermic effect.

Table 4. TGA data of PE

Sample	T_m , $^{\circ}\text{C}$	Thermal degradation stages				T_{max} , $^{\circ}\text{C}$
		I, exo	II, exo	III, endo	IV, exo	
PE1	132	<u>186-309*</u> 1.1	<u>309-421</u> 14.4	<u>421-522</u> 76.3	<u>517-581</u> 2.0	485
PE2	133	<u>188-321</u> 3.1	<u>321-428</u> 14.0	<u>428-520</u> 74.3	<u>520-579</u> 2.2	490

* In the numerators— temperature range in $^{\circ}\text{C}$, in the denominator - weight loss in this temperature range (%).

Comparison of thermal analysis data of PE specimens indicates that the PE specimens are characterized by almost identical thermo-oxidative destruction stages; PE2 specimen is characterized by higher content of low-molecular fraction, as well as the presence of weak bonds.

In turn, temperature zone of thermo-oxidative degradation of oil fillers in Table 5 can be divided into three range, namely, 20-400, 400-500, and 500-770 $^{\circ}\text{C}$. At the first stage (temperature range is 20-400 $^{\circ}\text{C}$), there is evaporation of hydrocarbons, oxidation of methylene and methyl groups, and decomposition of carboxylic groups. At the second

stage (temperature range is 400–500 °C), there is subsequent decomposition of the carboxyl–carbonyl groups, cleavage of peripheral groups from aromatic structures, and probably the condensation [40] of aromatic rings. At third stage (temperature range is 500–770 °C), there is a combustion of condensed naphthene-aromatic structure.

Table 5. TGA data of petroleum fillers

Sample	Mass loss/mass% in temperature interval			A	F	P
	Δm_1 20–400°C	Δm_2 400–500°C	Δm_3 500–770°C			
asphalt	18.1	42.8	39.1	1.6	0.22	1.1
asphaltenes	8.4	42.4	49.2	1.0	0.09	0.9
resins	20.7	47.3	32.0	2.1	0.26	1.5

To characterize oil fillers, we used the parameter $A = (\Delta m_1 + \Delta m_2) / \Delta m_3$, which characterizes the ratio of sum of paraffin–cycloparaffin hydrocarbons and alkyl substituents to naphthene-aromatic structures, $F = \Delta m_1 / (\Delta m_2 + \Delta m_3)$, which reflects the mass ratio of light and medium components to heavy, and $P = \Delta m_2 / \Delta m_3$, which reflects the mass fraction of peripheral substituents in cyclic structures [41].

Analysis of TGA data showed that asphaltenes are characterized by the highest thermal stability and the maximum weight loss occurs at the temperature higher than 400 °C. On average, asphaltene molecule contains less aliphatic structures, as well as lateral substituents in condensed naphthene-aromatic structures. Resins contain a larger number of alkyl substituents (A), while the weight fraction of peripheral substituents (P) in cyclic structure is almost two times as large as that in asphaltenes. The parameters in the case of asphalt containing asphaltenes and resins, as well as saturated and aromatic hydrocarbons in Table 1, are intermediate in Table 5.

Because asphaltenes and resins are formed by a continuous series of various hybrid high-molecular compounds of oil, only average molecular weight of these oil components can be considered. The average molecular weight is 1700 a.m.u. in the case of asphaltenes and 600 a.m.u. in the case of resins according to MALDI mass spectra. In the case of the resins isolated from asphalt in Table 1, the average molecular weight is highest, 819 a.m.u., while in the case of asphaltenes it is 1700 a.m.u.

It is mentioned in [22] that the structures, in which the hydrogen-to-carbon ratio (H/C) is less than 1.40–1.30 according to elemental analysis data, are preferred as fillers of composition materials. In our case in Table 2, the H/C ratio in asphalt is 1.36, while it is 1.25 in asphaltenes and 1.41 in resins.

3.2. Physicomechanical Properties

It was indicated [23, 24] that most physicomechanical properties worsen at high degree of filling of the polymer matrix with asphaltenes; therefore, we prepared the compositions with 4 wt % of asphalt and 4 wt % of asphaltenes. To determine the effect of resins on the characteristics of the compositions, we used additives at small quantities, namely, 0.1 and 0.2%, and also considered their effect in asphalt (1.6% of resins calculated from Table 1). We also presented some data for HDPE trademarks*, which already contain industrial additives (including 0.2 wt % of Anox® 20 Powder stabilizer). The specimens prepared from PE with 0.2 wt % of Anox and 0.2 wt % Anox with 4 wt % of asphaltenes were also compared.

The studies showed that the change of physicomechanical characteristics of the compositions does not have a clear dependence on their composition in Table 6.

Table 6. Physicomechanical properties of polyethylenes and their compositions

Samles (% wt)	TS, MPa	ε , %	E, MPa	σ , MPa	MFR, g/10min	ρ , g/sm ³
HDPE1*	>21*	> 500*	not regulated	not regulated	> 0.1* 6.32**	0.96**
PE1	35.1	1068	416	26	0.049	0.96
PE1 + Anox (0.2)	30.7	895	407	27	0.044	0.96
PE1 + asphalt (4)	29.7	850	580	29.7	0.16	0.963
PE1 + asphaltenes (4)	26.8	663	506	26.7	0.16	0.963
PE1 + asphaltenes (4) + Anox (0.2)	25.5	850	434	25.4	0.18	0.963
PE1 + asphaltenes (4) + resins (0.2)	27.8	770	541	28.4	0.15	0.963
PE1 + resins (0.2)	28	760	459	29.1	0.12	0.956
PE1 + resins (0.1)	29.1	770	507	29.6	0.11	0.958
HDPE2*	>30*	not regulated	not regulated	> 26*	>2.3*	0.957–0.963*

PE2	27.3	1130	420	26	0.572	0.954
PE2 + Anox (0.2)	27.4	968	411	27.3	2.352	0.96
PE2 + asphalt (4)	33.5	782	823	33.4	3.0	0.968
PE2 + asphaltenes (4)	26.8	753	462	31.1	3.01	0.968
PE2 + asphaltenes (4) + Anox (0.2)	27.7	761	557	31.4	3.07	0.97
PE2 + asphaltenes (4) + resins (0.2)	30.6	770	619	32.7	3.0	0.96
PE2 + resins (0.2)	34.8	750	670	35.2	2.7	0.96
PE2 + resins (0.1)	34.2	749	683	34.2	2.85	0.961

* Manufacturing requirements of HDPE trademark.

** Experimental values of HDPE trademark.

One example is that an increase in the elastic modulus (E) of polymers with the addition of disperse and not only disperse filler is not surprising and is a universal feature of all the composition systems. This occurs due to the fact that the elastic modulus of solid and unrelated filler particles is higher than the elastic modulus of polyethylene. It is evident that replacement of the fraction of bulk polymer with other particles decreases the strain capacity of the composition and increases its resistance to deformation.

An increase in the elastic modulus is also often associated with the presence of adsorbed polymer macromolecules on the surface of filler particles. One part of the macromolecule is adsorbed on surface and immobilized. This immobilization is transferred to a particular distance along the macromolecule decreasing its flexibility, which affects strain characteristics of the polymer composition. Consequently, a slight increase in the rigidity of polymer is observed with an increase in the filler content [23, 24].

It can be suggested that, in the case of PE1, interaction of polymer and filler is weaker at the interface, while in the case of PE2 compositions the presence of resins gives a more drastic increase in the elastic modulus E , in particular, in the case of asphalt in Figure 3.

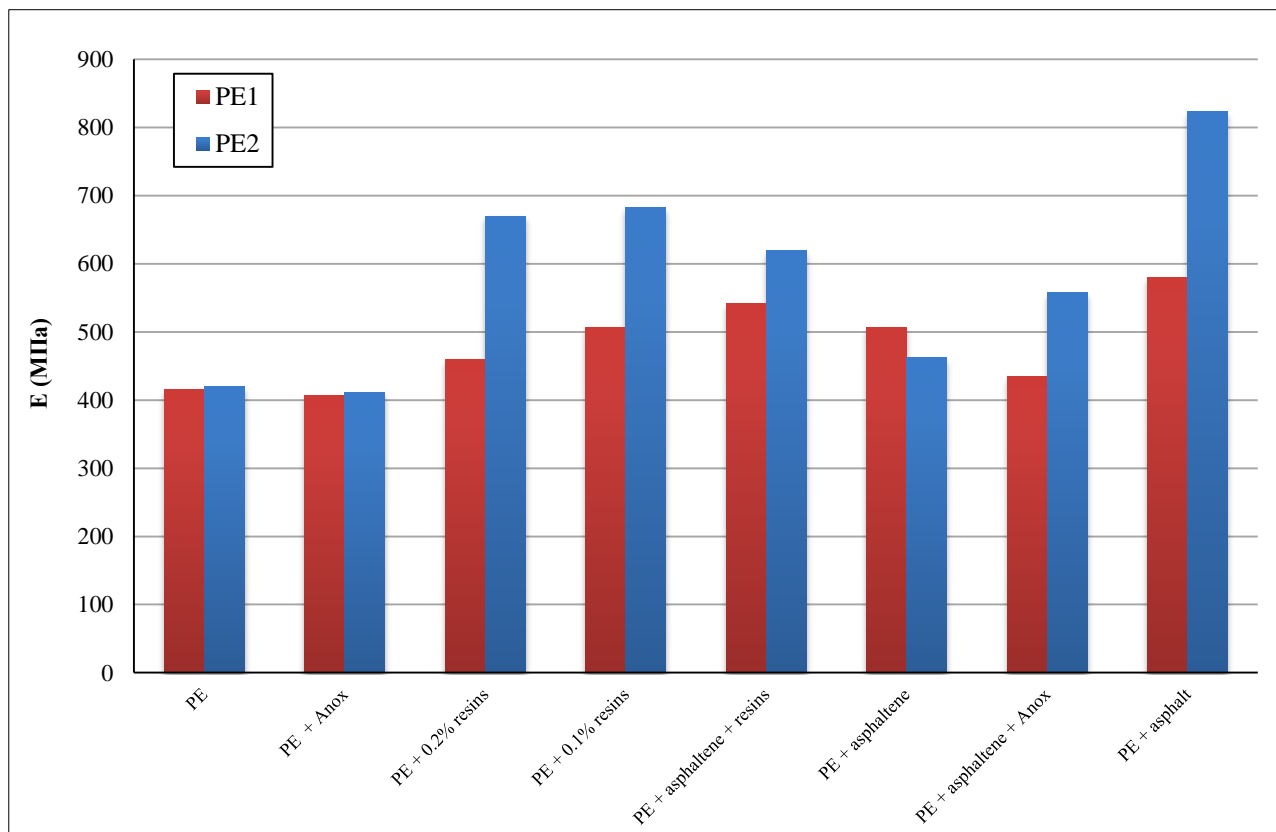


Figure 3. Effect of the composition of polyethylene compositions on elastic modulus (E)

Deformation of solid under external mechanical loads is caused not only by the change of the conformations of macromolecules, but also displacement of macromolecules relative to each other (flow). An increase in the tensile yield strength σ is observed almost for all PE compositions. It is clear from Figure 4 that the presence of resins, both individually and mixed with other components in the composition, increases the ductility of the polymer material. It is

known from the literature [17, 42] that petroleum resins are used to improve the ductility and adhesion of bitumen, as well as to reduce internal friction during processing (mixing, molding) of industrial rubber goods. The observed effect can also be associated with the structural features of petroleum resins' molecules, which have long alkyl chains and have surface-active properties [7, 10].

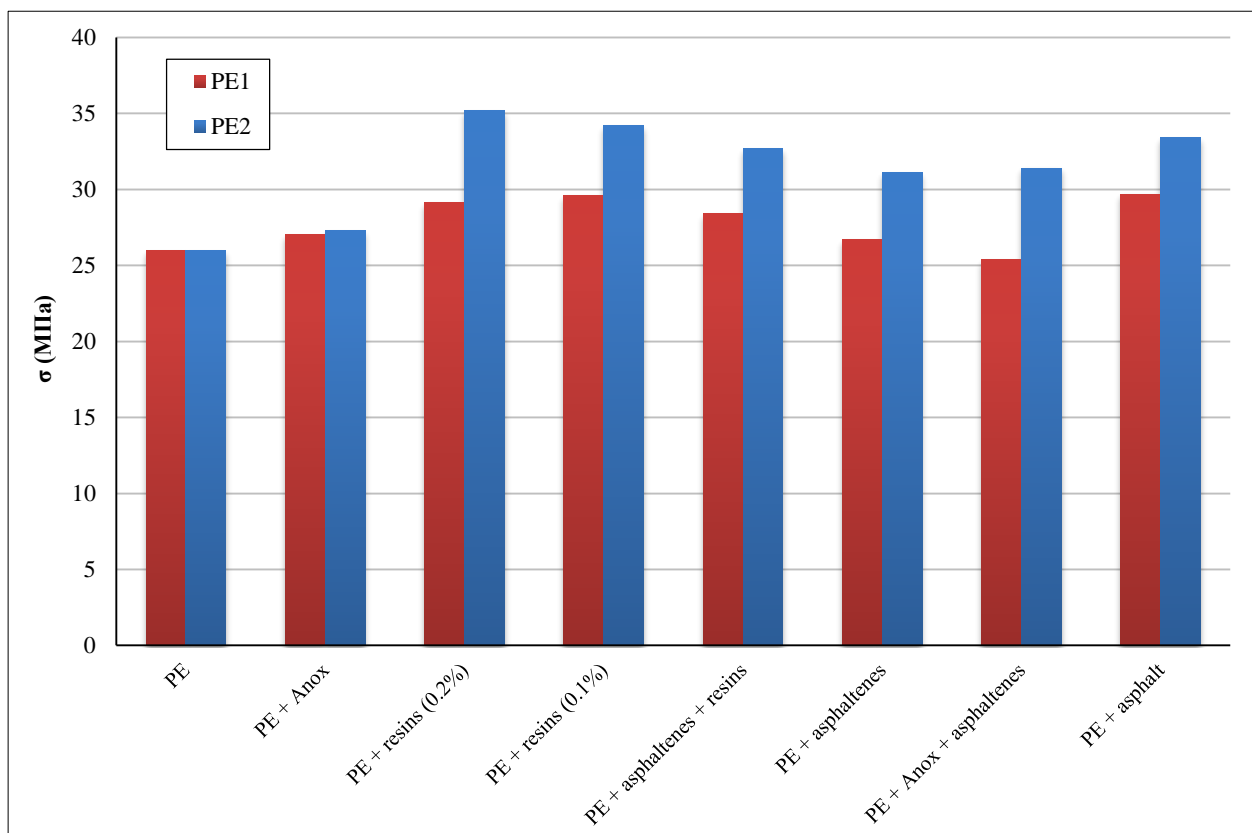


Figure 4. Dependence of Yield strength (σ) on the composition of polyethylene compositions

In the case of melt flow rate (MFR) parameter, there is a 4–6-fold increase as compared to the initial PE in Table 6. MFR is widely used in production and characterizes the viscosity of melts, average molecular mass, and the degree of branching of thermoplastics [43–46]. In this case, probably, the formation of many CH- π hydrogen bonds [47] initially occurs on both sides of a large number of polycondensed aromatic systems of oil fillers. This leads to a change in the spatial globular structure of polyethylene with the orientation of the macromolecules along the filler macromolecules, and, as a consequence, to an increase in the mechanical strength of the composite. When the temperature rises to 190 °C, during determination of the MFR, these intermolecular hydrogen bonds are destroyed, but due to the viscous-flow state of polyethylene, its spatial structure does not have time to return to its original state, which in turn leads to an increase in its fluidity.

Figures 5 and 6 demonstrate the tensile strength and elongation at break of the PE compositions. The best result is demonstrated by polyethylene compositions with asphalt, with resins and asphaltenes, with resins whereas, compositions with only asphaltenes show lower values. Probably, under given conditions for mixing, asphaltenes are insufficiently well distributed in the polymer material, forming small agglomerates [23–25], which are a source of stresses. Observed increase in strength (especially for PE2) can be explained by the plasticizing effect of resins, which also contribute to a better distribution of asphaltenes when used together in a polymer composition.

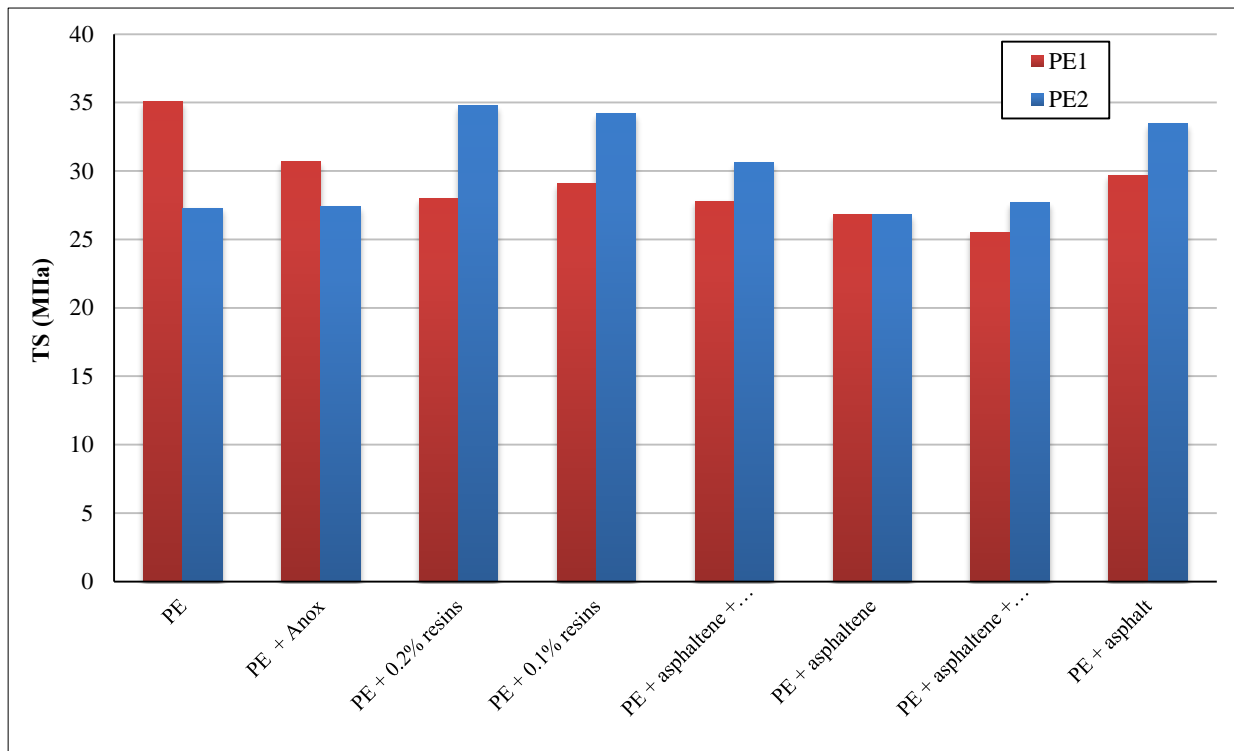


Figure 5. Dependence of tensile strength (TS) on the composition of polyethylene compositions

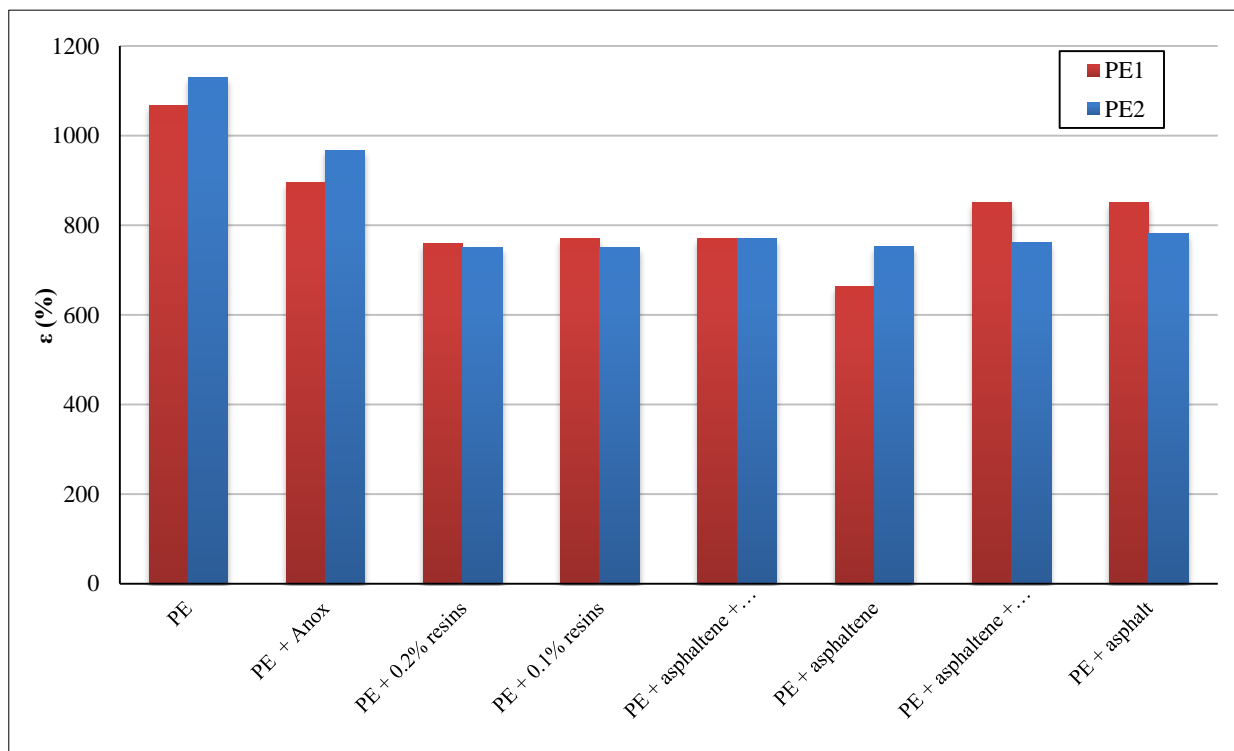


Figure 6. Dependence of elongation at break (ϵ) on the composition of polyethylene compositions

3.3. Thermo-oxidative Degradation

The effect of resin-asphaltene substances on the performance characteristics of liquid fuels, oils, and polymers were carried out in [48-50]. Analysis of the results of inhibition effect of oil stabilizers (OSs) in the model oxidation reaction of cumene showed that they include nearly 10% of high-performance stabilizers [48]. It was determined that the most effective fraction of OS contains the largest fraction of high-condensed aromatic structures with heteroatomic groups.

Investigation of thermal destruction of polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), and synthetic rubbers confirmed high performance of asphaltenes as stabilizers [23-25,48]. In this case, the price of OSs is

several orders of magnitude less than that of synthetic stabilizers as exemplified by Anox and other phenolic antioxidants.

The performance of the oil fillers as stabilizers of thermo-oxidative destruction was analyzed according to the accumulation rate of carbonyl groups in the oxidized polymer using IR spectrophotometry data, as well as TGA method.

In Figures 7 to 10, the dependences of the oxidation level of the PE composition calculated according to the ratio of relative intensities of the compositions at 1720 cm^{-1} (C-O bond of ketone and aldehyde types) to $1366\text{--}1368\text{ cm}^{-1}$ (CH_3 -groups) and 1305 cm^{-1} (CH_2 -groups) in IR spectra vs. time of thermal oxidation of the compositions are given.

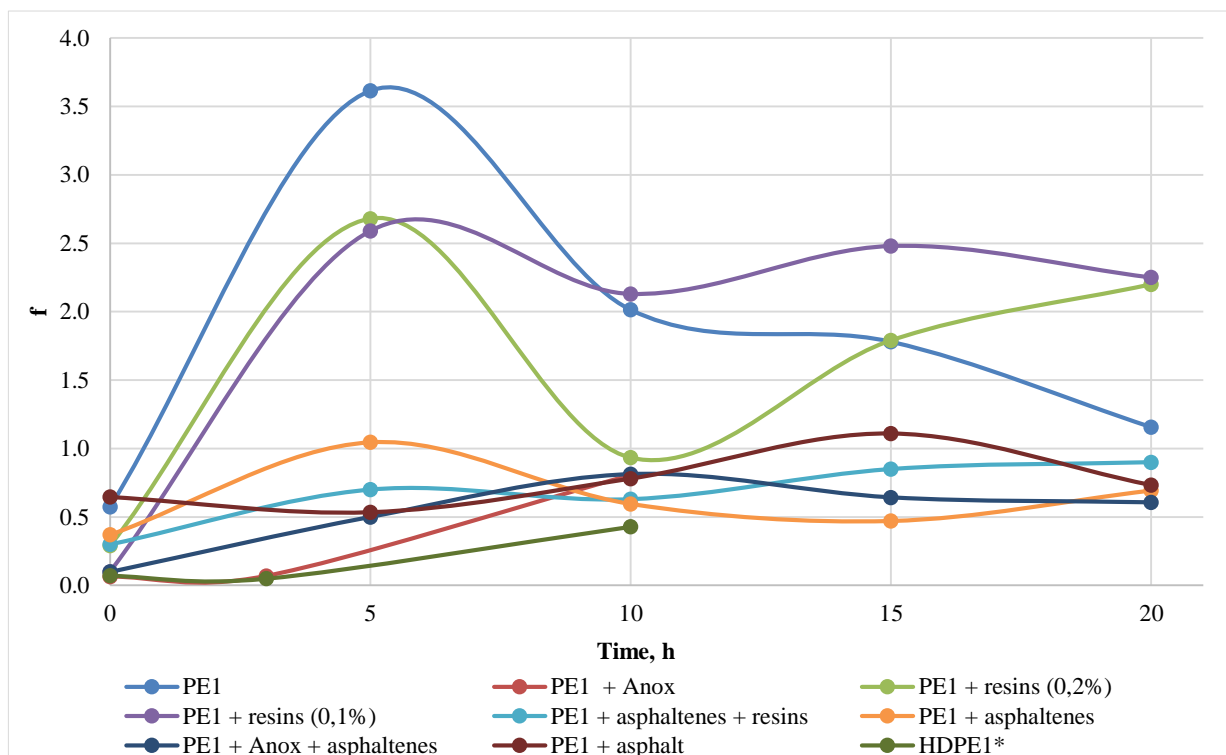


Figure 7. Dependence of the oxidation level f of PE1 compositions (I1720/I1366-1368) on the time of thermal oxidation

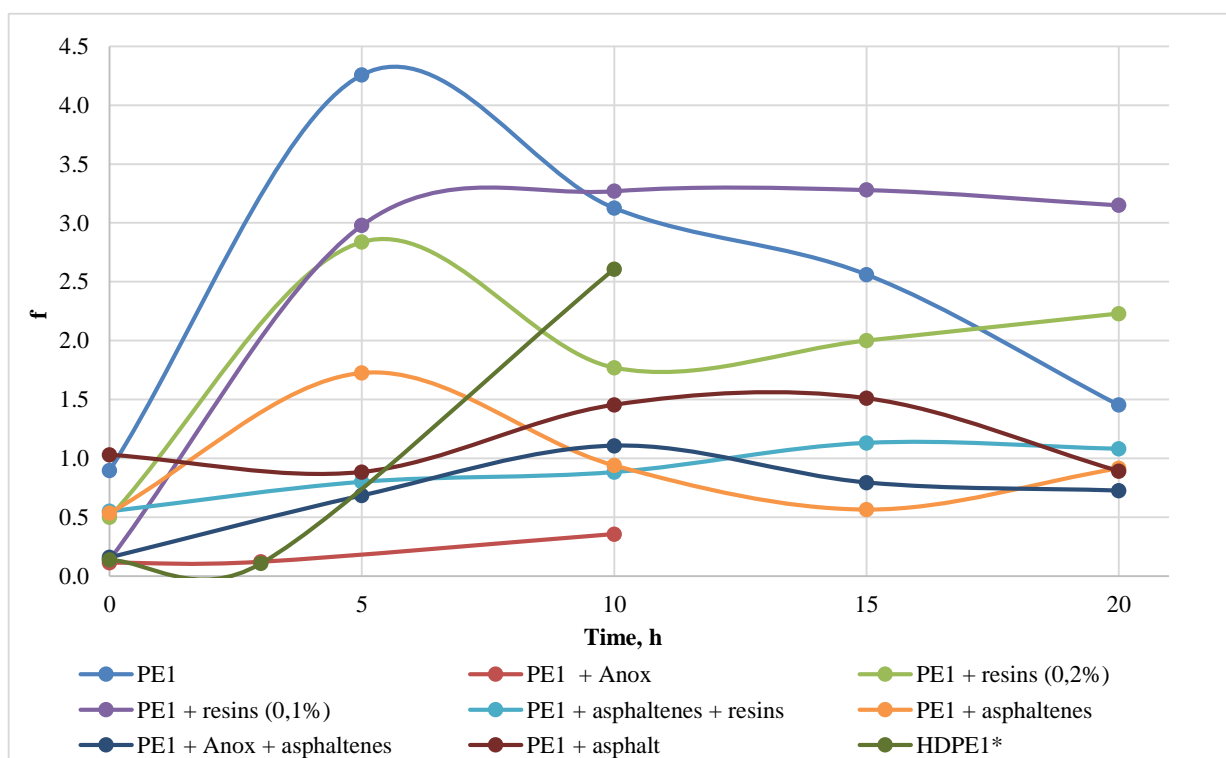


Figure 8. Dependence of the oxidation level f of PE1 compositions (I1720 / I1305) on the time of thermal oxidation

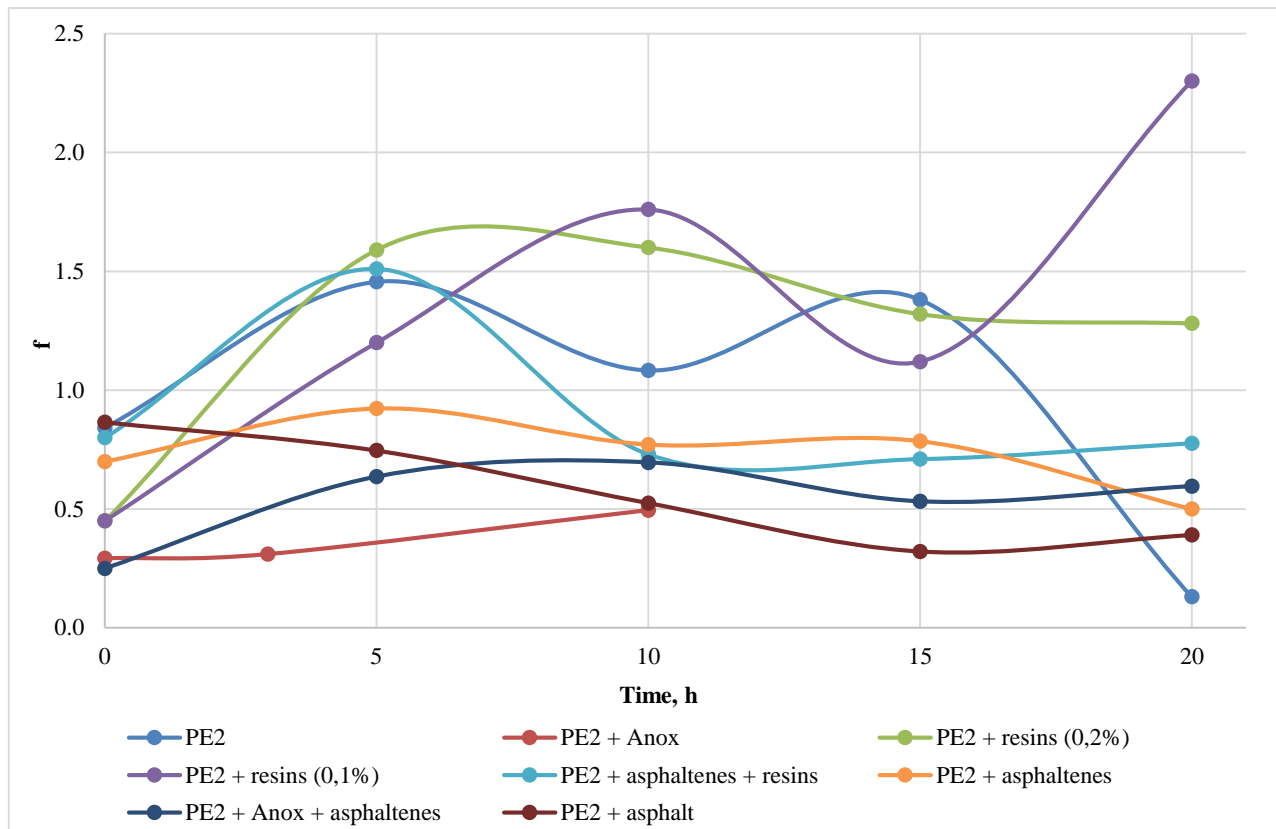


Figure 9. Dependence of the oxidation level f of PE2 compositions (I1720 / I1366-1368) on the time of thermal oxidation

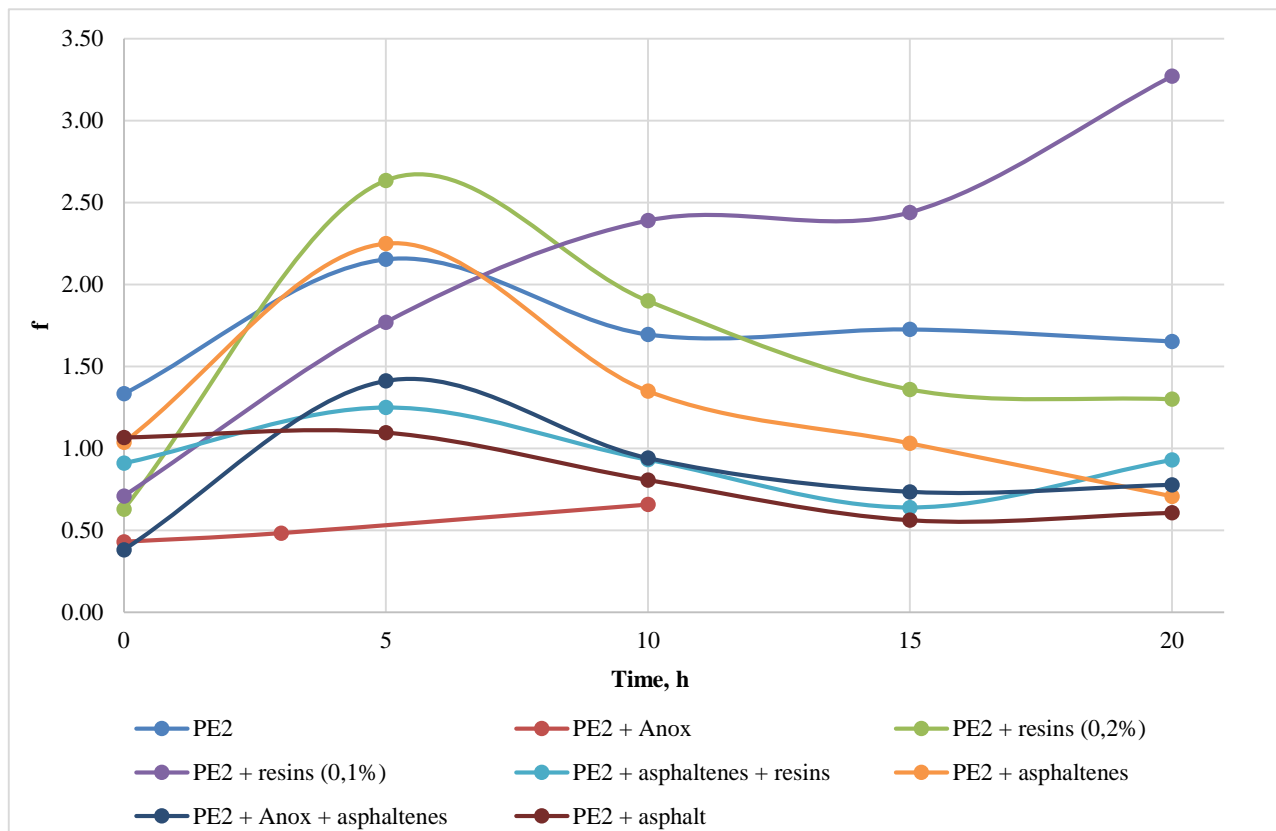


Figure 10. Dependence of the oxidation level f of PE2 compositions (I1720 / I1305) on the time of thermal oxidation

As a result, it was determined that resins do not stabilize polymer. On the contrary, the compositions containing asphaltenes, asphalt, and asphaltenes with resins demonstrate high thermal stability, which is comparable to that of the compositions of initial polyethylenes with Anox and industrial trademarks HDPE* containing stabilizers. It has been

established that inhibiting ability of thermo-oxidative processes is associated with the number of paramagnetic centers in the stabilizer molecule [17]. Due to the presence of paramagnetic centers, resins and asphaltenes are recommended as polymer stabilizers, while the number of paramagnetic centers and the rate of inhibition constant of the latter are 1-2 orders of magnitude higher.

The form of the change of the oxidation level (f) of all compositions with OSs on time is nonlinear. The first peak of f (at the times of thermo-oxidative destruction under study) appears at 5 h; then, it decreases in most cases and, after that, the second peak appears at 15 h; finally, this value decreases in all compositions. The specimens stabilized with Anox, on the contrary, firstly demonstrated the maximum protective effect; however, the oxidation level of the specimens increased with an increase in the ageing period of the polymer.

It is considered that phenolic antioxidants act as H donors and prevent the formation of hydroperoxide sequences and cleavage of primary bonds assuming that their concentration in the polymer remains higher than critical value. However, consumption of stabilizer at long-term ageing is intrinsic for them [51]. On the contrary, OSs are multifunctional, which is caused by the presence of condensed naphthene–arene structures, as well as heterofunctional groups [48, 50]. A long-term slowdown of radical processes, which is caused by the activation of inhibiting centers with oxygen and temperature, and formation of secondary inhibitors are intrinsic for them [50].

In analogy, high thermal stability according to TGA data is observed in all compositions of PE with fillers, except for the compositions with resins in Table 7. Though asphaltenes are considered best OSs [17, 48], asphalt exhibits comparable protective properties at the same order ($T_{5\%}$, $T_{10\%}$, and $T_{50\%}$).

Table 7. Data of thermal analysis of the compositions

Sample (wt.%)	T_m , °C	$T_{5\%}$	$T_{10\%}$	$T_{50\%}$
HDPE1*	127	355	385	479
PE1	132	266	344	466
PE1 + Anox (0.2)	134	359	407	486
PE1 + asphaltenes (4)	131	315	373	469
PE1 + asphalt (4)	128	331	369	469
PE1 + asphaltenes (4) + Anox (0.2)	129	322	371	486
PE1 + asphaltenes (4) + resins (0.2)	127	310	348	470
PE1 + resins (0.1)	127	280	340	470
PE1 + resins (0.2)	125	309	352	464
HDPE2*	138	274	340	472
PE2	133	321	376	462
PE2 + Anox (0.2)	139	367	414	488
PE2 + asphaltenes (4)	137.5	301	370	482
PE1 + asphalt (4)	130	300	391	478
PE2 + asphaltenes (4) + Anox (0.2)	138	362	410	486
PE2 + asphaltenes (4) + resins (0.2)	135	327	376	464,5
PE1 + resins (0.1)	133	316	377	469,5
PE1 + resins (0.2)	130	300	356	466

* Manufacturing requirements of HDPE trademark.

4. Conclusions

- Studies of the HDPE and PHMOC compositions have shown that introduction of up to 4% of filler to the polyethylene matrix does not significantly change physicochemical properties, while some parameters have shown an increase.
- It has been determined that addition of asphalt and asphaltenes both individually and in the mixture with resins to polyethylenes does not require stabilization of the composition using stabilizers of thermo-oxidative destruction.
- Comparison of the oil fillers has demonstrated that resins cannot be employed as individual additive, while asphaltenes possess some drawbacks, which are related to nonhomogeneous distribution in the polymer matrix. At the same time, resins provide higher dispersion of asphaltenes in the polymer matrix and improvement of viscoelastic characteristics of the composition and asphaltenes results in the stability of the composition to thermal destruction. Employment of the oil fillers containing both asphaltenes and resins is optimal.

- Results of experimental studies indicate that industrial residue of propane–butane deasphalting of tar, more specifically, asphalt containing asphaltenes and resins, is a promising filler and low cost of this stock renders it perfect source for the industry of polymer materials.

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6. Conflicts of Interest

The authors declare no conflict of interest.

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