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Polyolefin Composition Materials Filled with Oil Asphaltenes and their Functionalized Derivatives

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Abstract. In this work, composite materials based on LLDPE and asphaltenes, their functionalized derivatives, and an industrial residue of solvent deasphalting of tar were investigated. Physicomechanical, thermal and electret properties of composite materials were studied. The behavior of the compositions during melting and crystallization was studied by DSC, and crystallinity degree was calculated. The dispersion of oil fillers in a polymer matrix was investigated using SEM.

Keywords: LLDPE, filler, composition, heavy oil residues, asphaltenes, sulfonation, properties.

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Полиолефиновые композиционные материалы, наполненные нефтяными асфальтенами и их функционализированными производными

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Аннотация. В данной работе исследованы композиционные материалы на основе ЛПНП и асфальтенов, их функционализированных производных и промышленного остатка сольвентной деасфальтизации гудрона. Были изучены физико-механические, термические и электретные свойства композиционных материалов. Методом ДСК изучено поведение композиций при плавлении и кристаллизации, рассчитана степень кристалличности. С помощью СЭМ исследована дисперсия нефтяных наполнителей в полимерной матрице.

Ключевые слова: ЛПНП, наполнители, композиционные материалы, тяжелые нефтяные остатки, асфальтены, сульфирование, свойства.

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Introduction

Heavy oils and industrial oil residues in increased quantities contain asphaltenes – polycondensed high molecular weight heteroatomic compounds that complicate oil production and refining processes. At the same time, due to their structural features, they can be used to obtain a large amount of valuable materials. Nowadays, it is known that ion exchangers, sorbents, catalysts and various carbon materials can be obtained based on asphaltenes [1-6]. Asphaltenes are also actively used for filling polymers and obtaining various composites [7-9]. However, asphaltenes have a threshold concentration, the excess of which leads to the formation of small agglomerates that are sources of stress in composite materials [8, 9]. To improve the filling of polymeric materials, the compatibility of asphaltenes with the polymer matrix must be ensured.

Earlier, through the example of HDPE compositions with oil fillers it was shown that the combined use of asphaltenes and resins, as well as in the composition of industrial oil residues of solvent deasphalting (RSDA) of tar, is optimal for high dispersion in a polymer matrix [10]. Another way to improve the dispersion of the filler in the polymer matrix can be the modification of asphaltenes – the introduction of functional groups into their structure.

A simple method of asphaltenes functionalization is the effect of strong acids (sulfuric, nitric, etc.). Thus, the interaction of sulfuric acid with asphaltenes leads to the formation of not only sulfonic acid, but also hydroxyl and carboxyl groups [3, 8].

The work objective was to study the complex of properties of LLDPE compositions with oil fillers. The fillers were asphaltenes isolated from the tar, their functionalized derivatives and industrial residue of solvent deasphalting (RSDA) of tar. First, the physical and mechanical properties of polyethylene compositions, and the dispersion of fillers in the polymer matrix (by SEM) were estimated. Then the DSC method was used to study their behavior during melting and crystallization, as well as the change in the crystallinity degree. The effect of fillers on the electret properties of LLDPE was evaluated.

Experimental

Materials

As a polymer matrix in the composite material LLDPE of the 5118QM grade (PJSC "Nizhnekamskneftekhim") and oil fillers: RSDA, asphaltenes, sulfonated asphaltenes were used. RSDA is the industrial residue of propane-butane deasphalting of tar from PJSC ANK BashNeft Refinery Complex (Bashneft-Novoil).

Asphaltenes were extracted from the tar produced by PJSC TATNEFT (JSC TANECO) by precipitation using 20-fold excess of hexane, followed by filtration and extraction by hexane from coprecipitated resins and oils in a Soxhlet apparatus.

Sulfonation of asphaltenes (S-asphaltenes) was carried out as follows. A portion of asphaltenes (1 g) was dissolved in 100 ml of benzene until complete dissolution and formation of a homogeneous solution. Then a 20-fold excess of sulfuric acid, concentrated by weight, was poured and sulfonation was carried out at a temperature of 80 °C for 4 hours. Afterwards, an excess of water was added and the product was filtered off and dried.

Methods and equipment

Elemental composition was determined using a CHNS-O Euro EA3028-HT-OM analyzer (EuroVector).

Infrared (IR) spectra of the compounds were recorded in the range of 4000-400 cm^{-1} on a Vector-22 IR-Fourier spectrometer (Bruker) with the optical resolution of 4 cm^{-1}. Samples were prepared in tablets with KBr (Acros Organics 206391000). To study the structural and group composition of samples, spectral coefficients were calculated: $Al=D_{1450}/D_{1600}$ (aliphaticity), $Ar=D_{1600}/D_{720+1380}$ (aromaticity), $Cn=D_{1600}/D_{740+860}$ (degree of condensation), $Ox = D_{1700}/D_{1600}$ (degree of oxidation), $Sl = D_{1030}/D_{1600}$ (degree of sulfonation), $Hd = D_{3425}/D_{1600}$ (hydroxylity).

The preparation of the composition was carried out in the melt at the laboratory station Plastograph EC (Brabender, Germany) with adjustable electric heating at a temperature of 180 °C and a rotor speed of 50–150 rpm for 300 seconds. Fillers were introduced into the polymer matrix in an amount of 2.5; 5; 7.5%wt. Samples in the form of plates were made on a GT-7014-H10C thermo-hydraulic press (Gotech, Taiwan): the composition was heated to 180±5 °C, then pressure was applied, and after exposure under pressure (3 min), the samples were cooled without relieving pressure.

Tensile strength (TS), Elongation at break (ε), 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 2.16 kgs.

The scanning electron microscope Hitachi Tabletop Microscope TM-1000 with a solid-state backscattered electron detector at an accelerating voltage of 15 kV was used.

The DSC experiments were performed using the DSC204 F1 Phoenix differential scanning calorimeter (Netzsch, Germany) in an argon atmosphere (flow rate 150 mL min^{-1}) with the heating/cooling rate of 10 K min^{-1}. DSC was calibrated according to the manufacturer's recommendations by measuring six standard compounds (Hg, In, Sn, Bi, Zn, and CsCl). The 40 μL aluminum crucibles sealed with a pierced lid having a hole of 0.5 mm hole were used. Before the experiment, aluminum crucibles were annealed at 473 K for 30 min. For experiments, 14-20 mg samples of polymer were used. The degree of crystallinity X_{cryst} 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 [10].

The plates (2 mm) were electrified in a corona discharge field using an electrode consisting of 196 pointed needles equally spaced in an area of 49 cm^2 in the form of a square. The distance between the plate and the electrode was 20 mm, the voltage supplied to the corona electrode was 30 kV, and the polarization time was 30 sec. Before electretization, the plates were preheated in a furnace to 90-100 °C.

The surface potential V_s, the effective surface charge density σ_{ef}, and the electric field strength E of the samples were measured by the method of periodic shielding of the receiving electrode using an IPEP-1 electrostatic field meter located at a distance of 2 cm from the surface of the electret.

Results and discussion

Characterization of oil fillers. Asphaltenes in their pure state are not readily available industrial products, but they are concentrated in the residual heavy products of oil refining, such as tar. The study of the structure of asphaltenes, isolated from tar and their functionalized derivatives, according to elemental analysis (Table 1) and IR spectroscopy (Table 2) showed that the following structural group changes occur: a decrease in aliphaticity (Al), an increase in aromaticity (Ar), condensation degree (Cn), oxidation degree (Ox), sulfonation degree (Sl) and hydroxylity (Hd). That is, in S-asphaltenes, the content of -OH and C=O, S=O groups increases and the structure becomes more condensed in comparison with initial asphaltenes.

On an industrial scale, a source with a high content of asphaltenes is RSDA – a residual product of solvent deasphalting of tar after separation of deasphalted oil (DAO) [11, 12]. RSDA, in addition to asphaltenes (13.7%wt.), also contains resins (40.7%wt.), saturated and aromatic hydrocarbons

Table 1. Elemental composition of oil fillers

Sample	Content, wt.%				H/C
	C	H	N	S	
RSDA	83.78	9.62	0.25	5.17	1.38
asphaltenes	85.07	7.80	2.04	2.47	1.10
S-asphaltenes	61.06	4.60	0.80	9.72	0.90

Table 2. Structural-group composition of oil fillers according to FTIR data

Sample	Al	Ar	Cn	Ox	Sl	Hd
RSDA	3.35	0.37	0.95	0.32	0.63	0.96
asphaltenes	2.0	0.6	1.0	0.3	0.6	0.33
S-asphaltenes	1.05	0.86	1.3	0.48	1.03	0.88

(45.6%wt.) [10]. Elemental analysis data and structural characteristics of RSDA are presented in Tables 1 and 2.

Physicomechanical properties and SEM observations. The introduction of oil fillers into the LLDPE matrix in all cases leads to an increase in the tensile strength TS of materials (Table 3). The best result is demonstrated by polyethylene compositions with RSDA. Figure 1 shows the dispersion of filler particles in the LLDPE matrix and inhomogeneities of some particles are visible for samples filled with asphaltenes (1c) and S-asphaltenes (1d). According to SEM studies, the LLDPE composition with RSDA has the best dispersion in the polymer matrix.

The good dispersion of the samples with RSDA and the increase in the strength of the material can be explained by the plasticizing effect of resins, which are part of the filler and contribute to the better distribution of asphaltenes in the polymer matrix [10].

An increase in the elongation at break ε (Table 3) occurs for almost all polyethylene compositions, except for samples with S-asphaltenes. With the introduction of 7,5%wt. S-asphaltenes in LLDPE material becomes more brittle with lower elongation at break, while the yield strength σ is increased. Although for all other compositions the σ value is somewhat underestimated in comparison with the initial LLDPE.

MFR characterizes the viscosity of melts, and the indicator is used to select the technology for polymer processing. The introduction of RSDA into LLDPE leads to a slight increase in MFR, and, consequently, to a decrease in the melt viscosity. This can be explained by the presence of resinous substances in the filler, which reduce the internal friction of molecules and increase the plasticity of the material.

The introduction of asphaltenes into LLDPE leads first to a decrease in the viscosity of the polymer melt (2.5%wt. of a filler), and then to an increase (5 and 7.5%wt. of a filler). The introduction of S-asphaltenes leads to a significant increase in the viscosity of the polymer melt at all degrees of filling. This increase is presumably associated with the formation of rigid particles in the transitional layer of the melt with a reduced mobility, as a result of which the movement (flow) of molecules is impeded.

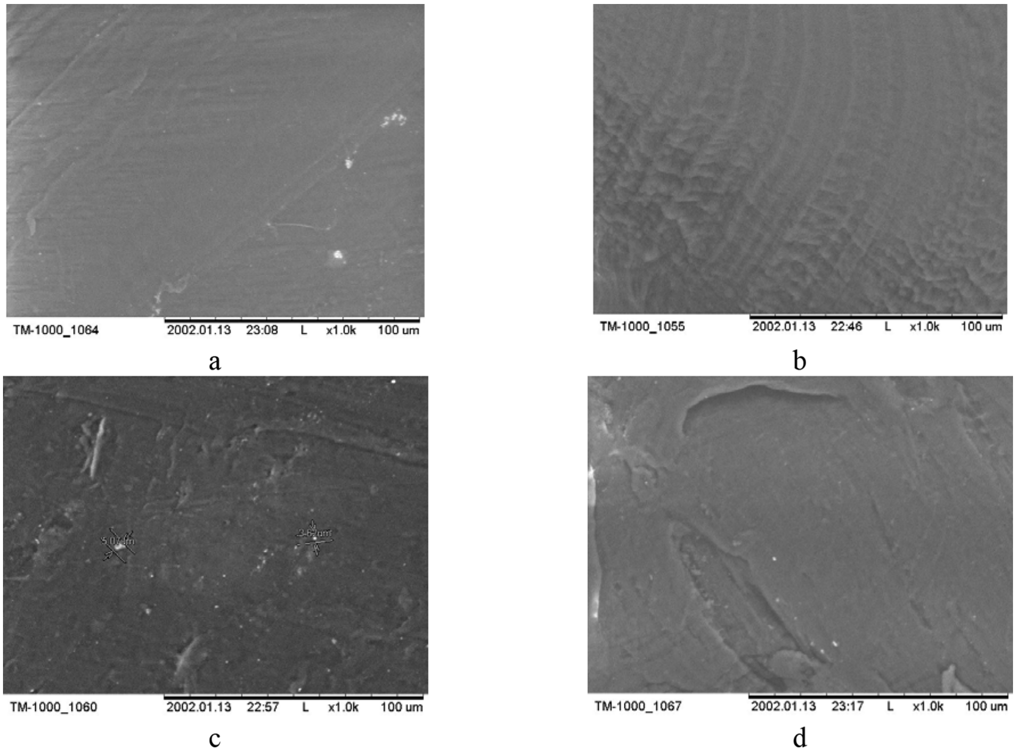
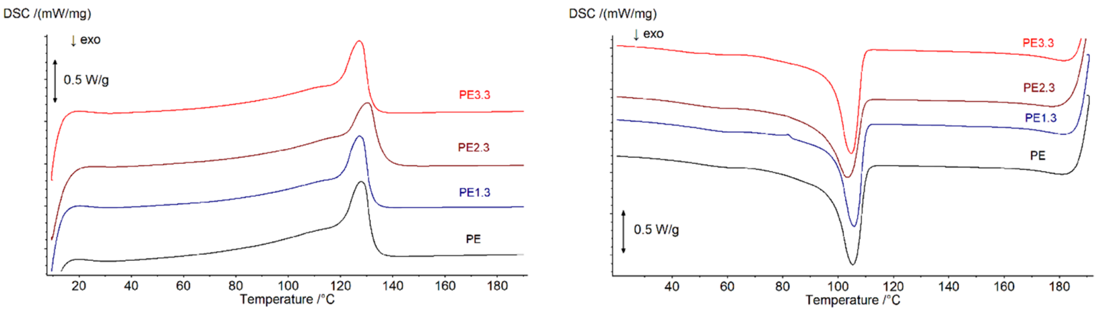


Fig. 1. SEM images of cross-sectional of LDPE (a) and composition with 7.5%wt. of fillers (RSDA (b), asphaltenes (c) and S-asphaltenes (d))

Table 3. Physicomechanical properties of LLDPE and compositions with oil fillers

Sample	TS, MPa	ε, %	σ, MPa	MFR, g/10 min
LLDPE	10.2	582.4	7.6	1.89
LLDPE + RSDA				
2.5%wt.	18.9	719.8	7.3	1.96
5%wt.	17.4	697.2	6.9	2.1
7.5%wt.	18.3	768.1	6.7	2.2
LLDPE + asphaltenes				
2.5%wt.	15.5	582.7	7.3	1.91
5%wt.	17.1	637.6	7.2	1.73
7.5%wt.	17.1	687.1	6.9	1.7
LLDPE + S-asphaltenes				
2.5%wt.2	14.4	537.4	7.5	0.51
5%wt.	14.3	559.6	7.5	1.21
7.5%wt.	13.7	497.5	7.9	1.7

Thermal properties. To study the melting behavior of LLDPE and all of its compositions, DSC thermograms were recorded, and results obtained at the maximum filling (7.5%wt.) are presented in Fig. 2. Peak melting temperatures T_m and total heat of melting ΔH_m obtained from the DSC curves for all samples are shown in Table 4. As seen, all curves are similar, and melting temperature for all



a b

Fig. 2. DSC thermograms of LLDPE (PE) and its composites with 7.5%wt. of oil filler (PE1.3 – RSDA, PE2.3 – asphaltenes, PE3.3 – S-asphaltenes) obtained during heating (a) and cooling (b)

Table 4. Results from DSC measurements, T_m melting peak temperature, T_c crystallization peak temperature, ΔH_m total heat of melting, ΔH_c total heat released during crystallization, X_{cryst} degree of crystallinity

Sample	T_m, ºC	ΔH_m, J/g	T_C, ºC	ΔH_{cryst}, J/g	X_{cryst}, %
LLDPE	127.9	121.2	105.4	83.9	41.36
LLDPE +RSDA					
2.5%wt.	127.4	115.0	105.6	78.58	39.25
5%wt.	127.1	116.5	105.8	80.57	39.76
7.5%wt.	127.3	109.5	105.8	78.34	37.37
LLDPE + asphaltenes					
2.5%wt.	126.1	116.8	107.1	77.27	39.86
5%wt.	127.5	120.2	105.8	84.48	41.02
7.5%wt.	130.4	114.9	103.5	78.03	39.21
LLDPE + S-asphaltenes					
2.5%wt.	128.0	102.5	105.4	77.65	34.98
5%wt.	127.8	107.8	104.2	75.94	36.79
7.5%wt.	127.2	108.7	104.8	80.55	37.10

samples is approximately the same – 127.5 °C, except for the sample filled with 7.5%wt. of asphaltenes (PE2.3 in Fig. 2), where the largest increase in T_m to 130.4 °C is observed. The lowest values of ΔH_m and crystallinity degree X_{cryst} are observed for LLDPE samples filled with 2.5%wt. of S-asphaltenes (Table 4).

Crystallization of the samples was also recorded upon cooling from the melt. The results are shown in Figure 2 and Table 4. Fig. 2 shows that the crystallization peak temperature is slightly shifted to lower values with the addition of 7.5%wt. of asphaltenes (PE 2.3). This means that asphaltenes have little nucleating effect on LLDPE crystallization. In general, for all filled polyethylenes, there is a decrease in total heat released during crystallization ΔH_c, due to the lower crystallinity X_{cryst} of the compositions compared to the initial LLDPE.

Electret properties. Polymeric materials have a number of properties important for electronics. They have a low specific weight, are easily processed and are chemically inert. Most polymers are insulators, so they are widely used as dielectrics and insulating materials. There is a possibility to create an electret state for dielectric polymers – to obtain an electret. Electrets can generate constant, relatively high electric fields for a long time without any additional power supplies and high-voltage converters [13].

It is important to study the electrical properties of polyethylene compositions with petroleum-derived dispersed fillers. It is known from the literature [14] that, due to the ability to absorb visible light, asphaltenes can be used as dyes to create dye sensitized solar cells (DSSC), where asphaltenes are a light absorber and photoreceptor sensitizing the conductor. Also, it should be noted that asphaltene fractions are a strong electron donor and acceptor. The paramagnetic phase of asphaltenes can be used as available semiconductors for nanoelectronics [15].

The compositions were electreted using the corona discharge method. It was found that the introduction of fillers such as RSDA, asphaltenes, and S-asphaltenes mainly leads to an increase in the electret properties, expressed on the graph by the surface potential index V (Fig. 3). Changes in the indicators of the effective surface charge density σ_{ef} and the electric field strength E occur similarly to the change in the surface potential. It was found that compositions filled with sulfonated asphaltenes are characterized by the ability to accumulate and maintain a charge, especially at a filling degree of 7.5%wt. (Fig. 3).

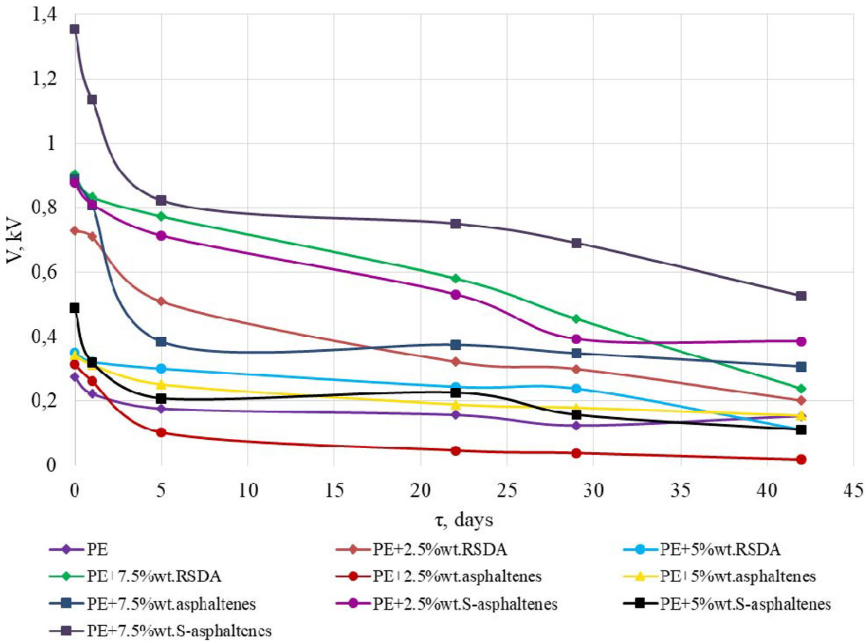


Fig. 3. The dependence of the surface potential on the storage time

An increase in electret properties upon the introduction of fillers into a polyethylene matrix is associated with the appearance of new structural elements capable of acting as traps for injected charge carriers [16]. It is believed that charge traps can be chemically active impurities, specific surface defects, adsorbed molecules, differences in the order of arrangement of molecules on the surface and in the volume. The phase boundary is characterized by a denser packing of polymer chains, retardation of molecular mobility, and the presence of energetically deeper traps for charge carriers in comparison with the polymer matrix outside the boundary layer [17].

Conclusion

The study of LLDPE compositions with oil fillers showed that the industrial product RSDA, containing asphaltenes and resins, is optimal for polymer filling. With the use of sulfuric acid functionalized asphaltenes, a significant increase in the electret properties of LLDPE is noted. These features are favorable for creating new highly stable electret materials based on them.

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