ANTICORROSIVE MATERIALS FOR PIPELINES OF OIL COLLECTION AND TREATMENT SYSTEM

Esentayeva A.[1], Nadirov K.[1], Zhantasov M.[1*], Nadirov R.[2], Ashimova T.[1]

[1]*M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan*
[2]*Al-Farabi KazNU, Almaty, Kazakhstan*

[*]**Corresponding author's e-mail:** manapjan_80@mail.ru

ABSTRACT

The issues of developing a technology for producing new materials based on domestic raw materials, in particular, based on polymer compositions with fillers, melt mixing in a laboratory multifunctional twin-screw extruder UR-TC with modular screws and a modular cylinder are considered.

A copolymer of ethylene with vinyl acetate (sevilen) was used as the most effective compatibilizer. In the preparation of the composition used: vegetable filler - straw, guzapay, husk; mineral filler - wollastonite or carbon black; cementitious additive - cotton tar; low density polyethylene.

It was established that the degree of crystallinity of the filled composites is different, which is due to the different degree of dispersion of vegetable fillers. The adhesion was studied for systems of the type "polyethylene-savilen-fillers-tar" in various combinations and variations, the obtained data indicate an increase in adhesion with an increase in the concentration of sevilen to 15%. An increase in the concentration of vegetable filler also increases adhesion, but only to a filler content of 30-35%. From mineral fillers, an increase in adhesion causes wollastonite at a concentration of 5–9 wt. % the addition of tar additionally increases adhesion by 10-15%

It has been established that all composites containing fibrous substances fillers have approximately the same viscosity, the infusion of sevilen, whose viscosity is noticeably lower than that of polyethylene, reduces their viscosity to the composites, and the addition of tar does not affect this indicator.

Key words: oil, pipelines, guzapay, sevilen, transportation, low density polyethylene (LDPE), mineral filler

INTRODUCTION

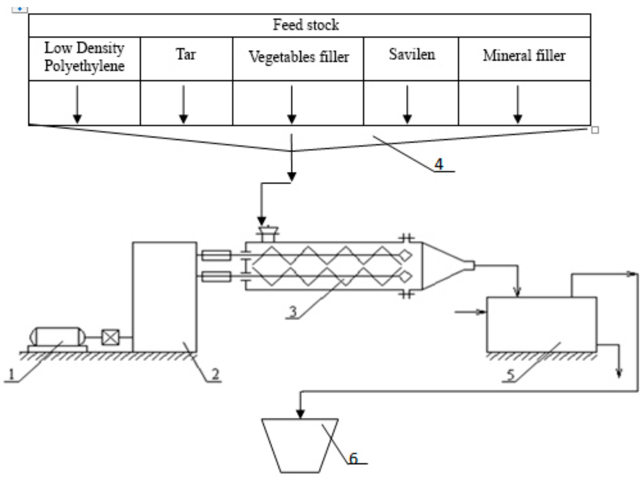
Delivery of oil, petroleum products and gas from oil wells to consumers is carried out mainly through pipelines, since this method is the most effective and safe way to transport them over long distances. Pipes are one of the key components in the structure of oil and gas equipment; they combine individual components of the technological chain into a single production complex [1-3]. Increased hydrocarbon production requires further development of the oil and gas transportation infrastructure. Indisputable is the fact that the reliability of pipeline transportation systems is a factor in the stability of the country's economy, as it allows the state to regulate the supply of energy to the external and internal markets [4]. It is known that one of the main problems facing humanity is the saving of natural resources, the search for their substitutes. Therefore, the losses caused by corrosion are particularly acute. In all industrialized countries, they account for 5–10% of the country's national income. The main corrosion loss is a premature failure of metal structures, the cost of which is much higher than the cost of the metal used. The second largest item of expenditure - a complex of measures to combat corrosion. To ensure the durability and trouble-free operation of pipelines, a system for their anti-corrosion protection has been developed and implemented [5,6]. As the analysis of the state of existing pipelines shows, one of the main problems of trunk pipelines is the mismatch between the service life of the used insulation materials and the service life of the pipeline [6,7]. Despite the considerable efforts of scientists all over the world in the fight against corrosion, the development of effective ways to protect existing trunk pipelines from corrosion damage is still one of the main tasks of pipeline transportation.

Today, the intensity of innovation activity is largely reflected in the level of economic development: in the global competition, those countries that provide favorable conditions for innovation benefit. The results of the analysis show that in order to transition to “sustainable innovative development”, Kazakhstan needs to combine the development of breakthrough technologies with a concentration of efforts on “industrial-innovative development”. It is breakthrough technologies that will be the main factor for Kazakhstan’s entry into the group of technological leaders. Among the priority technologies are the progressive technologies of mechanical engineering, including the use of new materials, in particular, technologies for protecting materials from mechanical effects (surfacing, spraying, lining of the protective layer) and chemical exposure (anti-corrosion coatings, paintwork, oxide), as well as advanced technologies in chemistry and petrochemistry , in particular, technologies for the processes of obtaining polymers and elastomers (polyethylene, polypropylene, synthetic rubber). Among the various options for anti-corrosion coatings to protect pipelines from corrosion, insulation with polymeric materials occupies a large place [8]. The most effective from the point of view of reliability is the insulation, which is, as a rule, two-layer or three-layer polymer structures based on polyolefins and polyepoxides. But the production of most of them is based on imported raw materials. The available domestic materials are still not widely used in the corrosion protection of critical pipelines. However, the need to successfully compete with foreign counterparts and the constantly growing level of technical requirements on the path to "industrial-innovative development" necessitates improving and expanding the range of compositions used in the plant and route corrosion protection of pipelines. One of the ways to solve this problem is the development of new materials based on domestic raw materials [8,9].

MATERIALS AND METHODS

The main problem that arises when trying to improve the mechanical characteristics of low density polyethylene (LDPE) by infusion fillers is associated with the need to ensure the transfer of force from the polymer matrix to the filler particles embedded in it. To achieve this effect, the filler particles must be evenly distributed in the polymer matrix. Not all fillers allow obtaining a fairly homogeneous system with a uniform distribution of particles in the material. This requires special treatment to improve the compatibility of filler particles with the polymer and their uniform distribution throughout the matrix [10]. The infusion of the compound in the LDPE is necessary to improve its properties: impact strength; heat resistance, modulus of elasticity, strength; increase resistance to the formation of surface cracks. As the most effective compatibilizer, a copolymer of ethylene with vinyl acetate (Sevilen), brand 11104-030 [11] was used. Vegetable filler - straw, guzapay, husk; mineral filler - wollastonite, aluminum oxide or carbon black; the cementitious additive - cotton tar and the rest is polyethylene.

Polymer compositions were obtained by melt blending in a laboratory multifunctional twin-screw extruder UR-TC with modular screws and a modular cylinder. The installation includes an extruder with dispensers, a cooling bath and a pelletizer. A schematic diagram of the laboratory setup is shown in Figure 1. A twin-screw extruder consists of cylinder 1, two screws 2, mechanical transmission 3, and an electric motor 4. The capacity of the extruder feed zone depends on the free volume between the two turns and on the uniformity of the material feed. In the extruder, the screws have five zones: the inlet zone (material pickup and preheating), the plasticization zone (heating and agglomeration), the compression zone (sealing the degassing zone and the plasticization support), the degassing zone (degassing of the melt, including the air outlet), and the exit zone (complete melting, homogenization and extrusion). In the entrance zone, the mixture is captured and preheated through internal and external friction, as well as heat transfer. In the plasticization zone, this process continues until the state when the powder of the mixture on the surface is so heated that it begins to agglomerate under the influence of mechanical energy. After the start of the agglomeration process and large agglomerates begin to form quickly, creating greater resistance to the cutting process. An important element of an extruder is a metering device, having, as a rule, a metering screw, with the help of which the precise adjustment of the supply of raw materials is carried out. The compression zone supports the plasticization process by further compaction of the agglomerate and increasing the back pressure in the direction of the plasticization zone. As a result of this pressure, the reverse flow of the mixture through the gap of both screws increases. In addition, the compression zone serves as a seal before the degassing zone. The function of the degassing zone in the removal of gaseous inclusions and trapped air from the plasticized (agglomerated) plastic material. After the degassing zone, the plastic material in the exit zone undergoes the final plasticization and sufficient pressure is created in it to force through the die plate. In a twin-screw extruder, shearing, rolling and chafing of the material is carried out efficiently.



1 - electric motor, 2 - mechanical transmission, 3 - screws, 4 - distribution mechanism for feeding raw materials (initial components), 5 - cooling of the composite, 6 - bunker for finished products.

Fig. 1. Diagram of the laboratory setup for the production of composites by extrusion

To determine the quality of the external polyethylene coating, the methods recommended by TU 1390-003-11928001-01 “Steel pipes with external anti-corrosion coating based on extruded polyethylene” were used:

The coating thickness was determined by a thickness gauge designed to measure the thickness of non-ferromagnetic coatings on the “K5 constant” ferromagnetic substrate.

After mixing all the components in a laboratory extruder and cooling the composite, the samples of the obtained material were ground using a knife mill. The crushed material was subjected to extrusion using a manual hydraulic press with an electronic unit to heat the plates. Pressing was carried out at a temperature of 150 °C and a load of 7 kN for 3 minutes with rapid cooling. As a result, film samples of circular shape with a diameter of 10 cm and a thickness of about 100 microns were obtained.

The effect of various fillers on the thermophysical properties of the polyethylene matrix was evaluated by differential scanning calorimetry.

RESULTS AND DISCUSSION

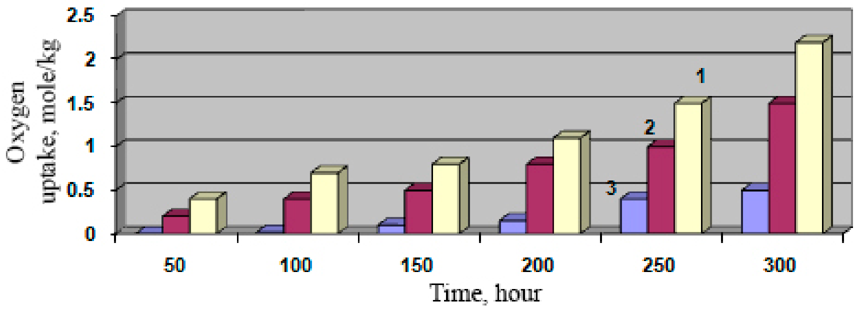
To study the processes associated with physical transitions, the samples were melted twice. Film samples were obtained by the method of thermopressing with rapid cooling. During rapid cooling, small crystallites are predominantly formed. In this regard, after the first melting in materials with slow cooling, larger and more perfect crystallites were formed, the melting point of which is higher than that of small crystallites. The obtained data indicate that the fillers used have a certain influence on the crystallization process. Apparently, the injected fillers act as nuclei of crystallization, therefore, the degree of crystallinity of materials with fillers is higher than that of pure polymer, and a directly proportional relationship is observed between the concentration of the filler and the measured parameter. With an increase in the concentration of vegetable fillers above 40 wt.%, the established dependences remain, however, the plasticity of the material obtained and its strength are significantly reduced. It was established that the degree of crystallinity of the filled composites is different, which is due to the different degree of dispersion of vegetable fillers. With the infusion of the composition of sevilen, the degree of crystallinity increases, and the melting point decreases, and there is a symbate dependence of these changes on the concentration of sevilen; % there is an inversely proportional relationship and the quality of the finished material, regardless of the type of filler, deteriorates in terms of mechanical properties.

The nature and concentration of the mineral filler does not have a noticeable effect on the degree of crystallinity, however, with an increase in the concentration of wollastonite and carbon black above 10 mass. %, the crystallization process changes its character, which gives incomparable results. The infusion of cotton tar to the mixture slightly increases the melting point and degree of crystallinity, and only to the tar content up to 1.5 mass. %, then there is a sharp jump in the nature of the changes in the studied parameters.

Based on the obtained results, a preliminary effective composition of polymer compositions was made:

- a vegetable filler - straw, guzapay, husk;
- mineral filler - wollastonite, aluminum oxide or carbon black;
- content of vegetable filler - 25-30 wt. %;
- content of mineral filler - 8-10 wt. %;
- content of sevilen (EVA) - 8 wt. %;
- tar content - 2–4 wt.%;
- polyethylene - the rest.

Further, the process of thermal oxidation of composites with fillers and tar in a solid state, that is, at a temperature below the melting point of polyethylene, was studied. The oxidation kinetics was studied at 90 °C with an oxygen pressure of 500 mm Hg. on a manometric unit with absorption of volatile oxidation products with potassium hydroxide [12]. It is established that all three fillers affect the oxidation process in different ways. The results of oxidation in the solid phase (Figure 2) indicate that the lower the density of the filler, the more intense the oxidation of the compositions. Apparently, the speed and intensity of oxidation is associated with the structure of the composite, loose (straw) filler leads to a better permeability of the material, which causes an increase in the rate of oxidative destruction, dense (guzapay) - on the contrary. Hence, we can conclude that during oxidation in the liquid phase, the speed of the process is determined by the chemical composition of the compositions, and during solid-phase oxidation, the morphology (structure) of all the materials studied plays the main role.

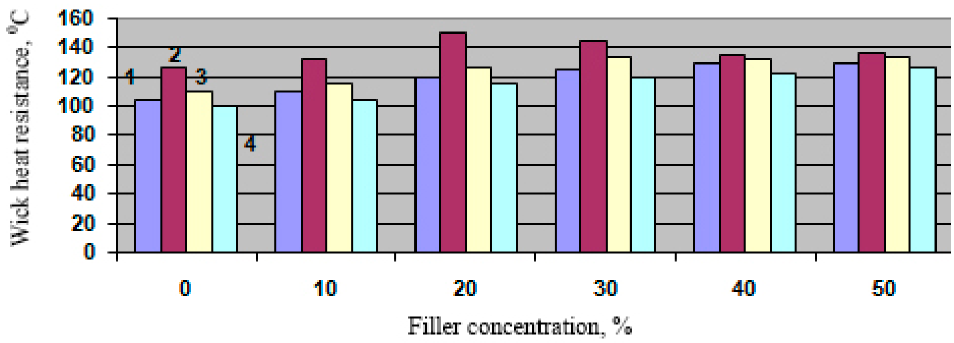


1 - straw, 2 - guzapay, 3 - husk.
Content, wt. %: Guzapay -30; wollastonite - 8; Savilen - 8; tar - 1;
LDPE - the rest.

Fig. 2. Dependence of the oxidation rate of composites at a temperature of 90 ° C and an oxygen pressure of 500 mm Hg. depending on their composition

The obtained dependences slightly change with the infusion of sevilen, the thermal stability of the composite slightly increases with the infusion of fillers. At the same time, thermogravimetric analysis of pure fillers indicates their lower thermal stability, even at temperatures above 400 ^{o}C, they almost completely decompose. It can be argued that in the composition of the polyethylene composite there is an increase in their thermal stability due to the formation of new strong bonds and a change in the structure of the material as a whole [13, 14].

As can be seen from the data of Fig. 3, with an increase in the concentration of vegetable filler, the heat resistance of the composite is increased by Vick heat resistance. Heat resistance is known to depend on the flexibility of the polymer chain; Obviously, with the infusion of fine particles of the filler in the polyethylene matrix, the flexibility of the polymer macromolecule chain decreases, which leads to an increase in the heat resistance of the composites. The increase in heat resistance of polymers with the infusion of fillers is also due to the fact that the additives themselves are sufficiently resistant to the temperatures studied. The nature of the mineral filler has a noticeable effect on Vick heat resistance: wollastonite increases this indicator by 17-21%, aluminum oxide only by 5-7%, and carbon black affects the studied indicator negatively, reducing it by 7-8%.



The concentration of the mineral filler - 7 wt. %
2 - wollastonite, 3-alumina, 4 - carbon black.

Fig. 3. The effect of the concentration of vegetable filler(guzapay) on heat resistance of composites of composition of LDPE + 8 wt. % EVA + 1.5 wt. % tar (1)

The presence of hydrophilic plant and mineral fillers in composites leads to an increase in their moisture and water absorption compared with the starting material. The moisture absorption of the film samples was determined as the ratio of the mass of the dry sample to the mass of the sample in air under standard conditions. GOST 4650-80 was adopted as the basis for the water absorption technique, but the exposure time of the samples in the aquatic environment was increased. The experiment was carried out for 60 days, which corresponded to the achievement of equilibrium water absorption by all materials. All samples in the air absorb is about 0.8-1.1 wt.% moisture without direct contact with water, the samples accumulate from the air, but this amount of moisture in the materials is not enough for active biodegradation. Water absorption of composites is determined by two factors: the water absorption of the fillers and the friability of the composite structure, which depends on the size and shape of the particles of the fillers. However, materials with guzapay are the most active in absorbing water, which is due to its increased hydrophilicity and the fact that the initial moisture was lower than that of other fillers. The nature of the mineral filler does not affect water absorption.

The adhesion was studied for systems of the “LDPE-SEBA-fillers-tar” type in various combinations and variations, the obtained data indicate an increase in adhesion with an increase in the concentration of SEBA to 15%. An increase in the concentration of vegetable filler also increases adhesion, but only to a filler content of 30-35%. From mineral fillers, an increase in adhesion causes wollastonite at a concentration of 5–9 wt. % the addition of tar additionally increases adhesion by 10-15%. As was shown above, a change in the number of fillers, compatibilizer and stabilizer leads to a change in the nature of intermolecular interactions. In the studied systems, zones of internal plasticization are observed, associated with changes in the volume of nodes of the structural lattice, and external plasticization, directly related to the increase in the distance between the nodes (Table 1). Melt flow rates were determined for the compositions obtained. The density of the film samples was determined by hydrostatic weighing (GOST 15139-69) using a VLR-200 analytical balance. The melt flow index was determined using the IIRT-5 installation, in accordance with GOST 11645-73. The test temperature is 190 ° C; the mass of the load is 5 kg. It has been established that all composites containing fibrous fillers (guzapay, straw, and husk) have approximately the same viscosity, the introduction of sevilen, whose viscosity is markedly lower than that of polyethylene, reduces their viscosity to the composites and does not affect the flow rate melt.

Table 1 - The influence of the composition on the amount of adhesion to steel

Type of subject sample	Composition				Adhesion, H/m^2
	Component content, masses.%				
	Filler		Savilen	Tar	
	vegetab.	mineral.			
LDPE	-		-	-	1427
LDPE	-	-	2	-	1496
			4	-	1546
			8	-	1789
			12	-	1876
			15	-	2032
LDPE + guzapay	10	-	8	-	1809
	20			-	1895
	30			-	1904
	40			-	1900
	50			-	1678
	35			0,1	1909
				0,5	1935
				1,0	1940
				1,5	2014
				2,0	2050
LDPE + guzapay + wollastonite	35	5	8	1,5	1950
		7			2242
		9			2135
LDPE + guzapay	35	5			1909
		7			1900
		9			1850

There is virtually no effect has nature and the investigated concentration of mineral additives. It was determined that the density of composite materials is about 1.02-1.11 g / cm^3, depending on the type of filler, which is higher than the density of pure polyethylene (0.95 g / cm^3). Obviously, this effect is explained by the more compact structure of the amorphous phase of the composite, including the filler. The introduction of SEBA into the composition does not significantly affect the density.

CONCLUSION

A technology has been developed to produce new materials based on domestic raw materials. Polymer compositions were obtained by melt blending in a laboratory multifunctional twin-screw extruder UR-TC with modular screws and a modular cylinder.

As the most effective compatibilizer was used a copolymer of ethylene with vinyl acetate (Sevilen) brand 11104-030. In the preparation of the composition were used: vegetable filler - straw, guzapay, husk; mineral filler - wollastonite or carbon black; the knitting additive - cotton tar; polyethylene - the rest.

It is shown that the degree of crystallinity of the filled composites is different, which is due to the different degree of dispersion of vegetable fillers. The adhesion was studied for systems of the type “PE-SEBA-fillers-tar” in different combinations and variations, the obtained data indicate an increase in adhesion with an increase in the concentration of Sevilen to 15%. An increase in the concentration of vegetable filler also increases adhesion, but only to a filler content of 30-35%. From mineral fillers, an increase in adhesion causes wollastonite at a concentration of 5–9 wt. % the addition of tar additionally increases adhesion by 10-15%

It has been established that all composites containing fibrous fillers (guzapay, straw, husk) have approximately the same viscosity, the introduction of sevilen, whose viscosity is markedly lower than that of polyethylene, composites reduce their viscosity, and the addition of tar, due to its low concentration does not affect melt flow rates.

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