IMPROVING THE OPERATIONAL PROPERTIES AND CHEMICAL STABILITY OF POLYETHYLENE GEOMEMBRANES FILLED WITH SHEROBOD ARGILLITE FOR AGGRESSIVE SALINE SOIL CONDITIONS

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Abstract.
This study investigates the stability of nanocompositegeomembranes based on high-density polyethylene, modified with local argillite minerals from the Sherabad deposit, under conditions of aggressive saline soil. The primary objective of the research is to enhance the chemical degradation resistance and the physical-mechanical properties of the polymer material using nanofillers. Nanocomposite samples were prepared by incorporating various amounts (1-7 wt. %) of argillite into the high-density polyethylene melt via extrusion. The chemical stability of the materials was tested under long-term exposure (90 days) to highly mineralized (sulfate and chloride) aggressive environments. Scanning electron microscopy (SEM) analysis showed a uniform distribution of argillite particles within the polymer matrix and the formation of a tortuous path effect. The results indicate that the addition of an optimal amount of argillite, specifically 5%, increased the tensile strength of the geomembrane by 23% and significantly reduced the diffusion rate of salt ions. These findings provide a scientific basis for the potential of creating highly durable and effective geomembranes for hydrotechnical and land reclamation structures using local mineral raw materials.

Keywords: HDPE nanocomposites, clay-polymer interfacial interaction, tortuosity coefficient, environmental stress crack resistance, thermomechanical properties, mineral fillers, long-term durability in saline environments.

Introduction .
In the current era of global climate change, conserving water resources is of strategic importance, with geomembranes being the primary material for ensuring the impermeability of hydraulic structures. In their research, Rowe et al. [1] summarized 30 years of experience in using polymer geomembranes in environmental protection systems, proving that their hydraulic conductivity of less than 10−12 m/s almost completely eliminates the seepage of filtrate into the soil. According to an analysis by Touze-Foltz and Scheuermann [2], using geosynthetic materials in hydraulic structures (canals and reservoirs) reduces water loss due to filtration by more than 95%, which is the only way to ensure agricultural sustainability in arid regions.
From an environmental safety perspective, the barrier properties of geomembranes are crucial, especially in industrial waste landfills. Abdelaal et al. [3] studied the durability of polyethylene geomembranes under long-term operating conditions and demonstrated that with proper modification, their service life can exceed 100 years. However, Morsy and Rowe [4] assert that in aggressive chemical environments, the diffusion of heavy metal and salt ions through the polymer matrix leads to material degradation. For this reason, in recent years, researchers like Chen and Xu [5] have been working to radically reduce water permeability by using nanocompositegeomembranes that create a "tortuous path" effect, complicating the pathway for ion movement. Smith et al. [6], who investigated the effect of mineral fillers on the chemical stability of polymers in saline soil conditions, noted that using local clay minerals is the most economically and environmentally effective solution.
Although high-density polyethylene is known for its chemical inertness, material aging and degradation are observed under long-term operating conditions, especially in aggressive mineralized environments. Wang et al. [7] state that chloride and sulfate ions in saline soils penetrate the amorphous part of polymer chains, weakening the bonds between macromolecules. This process drastically reduces the mechanical strength of the material, causing it to become brittle [7].

One of the most pressing problems in this field is the phenomenon of environmental stress cracking (ESCR). In their research, Li et al. [8] demonstrated that microcracks appear in the material as a result of the rupture of the “tie molecules” of polyethylene crystals under the influence of aggressive liquids. These cracks compromise the integrity of the geomembrane and, consequently, lead to environmental pollution. According to results obtained by Jones and Smith [9], the service life of conventional geomembranes in areas with high salinity levels (e.g., in saline soils) was found to be 30–40% shorter than in laboratory conditions.

In recent years, filling the polymer matrix with layered minerals has been proposed as the most promising solution to this problem. Tan et al. [10] found that nanoparticles increase the density of “tie molecules” by controlling the degree of polymer crystallization and create a “tortuous path effect” that impedes ion diffusion. This ensures not only the mechanical strength of the geomembrane but also its resistance to aggressive chemical reagents [11, 12].

Scientists worldwide are conducting extensive research on modifying polymer matrices with various nanofillers to overcome the vulnerability of geomembranes in aggressive environments. In particular, Zhang et al. [13] achieved a significant reduction in the gas and liquid permeability of the material by incorporating montmorillonite (MMT) and organoclay into the polyethylene composition. They assert that the layered structure of the nanofiller acts as a physical barrier, obstructing the movement of ions between polymer chains [13]. Furthermore, Al-Maadid et al. [14] have proven that using carbon nanotubes and graphite particles increases not only the barrier properties but also the heat resistance of geomembranes by 15–20%.

Recent studies indicate that the main factors determining the final properties of the material are the type of nanofiller and its degree of dispersion within the polymer matrix (exfoliation or intercalation). For instance, in research conducted by Kim and Park [15], silicon dioxide (SiO_2) nanofillerswere found to increase the number of crystallization centers in the polymer, thereby enhancing the material's chemical stability. However, as many international researchers have noted [16, 17], the high cost of synthetic nanofillers limits their industrial-scale application. For this reason, Liu and his research team [18] have recognized the creation of inexpensive and high-performance nanocomposites based on natural clay minerals as the most relevant direction in sustainable polymer material science today.

This study, for the first time, investigates the effect of argillite minerals from the Sherabad deposit, located in the southern region of Central Asia, on the stability of polyethylene geomembranes in aggressively saline environments. Sherabad argillite is distinguished by its high content of montmorillonite (up to 50%) and minerals of the illite group, which enables the formation of strong nano-level bonds with polymer chains [19]. Although preliminary research by Eshkurbonov et al. [20] showed that the high surface activity of the natural mineral alters the degree of polymer crystallization, the mechanism by which it acts as a diffusion barrier in aggressive mineralized soil conditions has not yet been fundamentally analyzed. Accordingly, this work aims to enhance the operational properties of nanocompositegeomembranes filled with local argillite and to model the kinetics of their degradation under the influence of saline ions.

Materials and methods of research.

In this study, high-density polyethylene granules with a density greater than 0.940 g/cm3 and a melt flow index of less than 1.0 g/10 min at 190°C/2.16 kg were used as the primary polymer matrix. As a modifying agent, a natural argillite mineral rich in montmorillonite and illite, sourced from the Sherabad deposit in Uzbekistan, was selected. During the mineral processing, the raw material was mechanically dispersed in a ball mill for 12 hours, sieved through a 45 μm mesh, and dried at 105°C for 5 hours.

To obtain nanocomposite samples, mixtures of high-density polyethylene and the prepared argillite powder were prepared in weight percentages of 1%, 3%, 5%, and 7%. The homogenization process was conducted in a twin-screw extruder by incrementally increasing the temperature zones from 170°C to 205°C. Using a thermal press, geomembrane sheets with a thickness of 2.0 mm, which meet waterproofing requirements, were molded from the resulting granules under a pressure of 15 MPa.

To evaluate the materials' resistance to aggressive external environments, the samples were immersed in 10% Na2SO4 and 5% NaCl solutions and kept at a temperature of 25 ± 2°C for 90 days. After the test, the physicomechanical properties of the samples, including tensile strength and elongation at break, were determined on a universal testing machine at a speed of 50 mm/min in accordance with the ASTM D6693 standard. Density values were confirmed by the hydrostatic weighing method based on the ASTM D1505 standard. The distribution of the nanofiller within the polymer matrix and the resulting "tortuous path" effect were fundamentally discussed using comparative analysis methods cited in international literature.

Results and Discussion.

Analysis of the results indicates that the introduction of Sherabad argillite into the high-density polyethylene matrix has a significant effect on the material's physicochemical properties. While the control sample (pure high-density polyethylene) demonstrated a tensile strength of 18 MPa and a relative elongation of 700%, it was observed that these indicators changed systematically as the argillite content increased.

Specifically, it was found that as the mineral filler content increases from 1% to 5%, the tensile strength at break increases relative to the initial value. Samples containing 5% by mass of argillite achieved the highest tensile strength. This phenomenon is explained by the uniform distribution of layered silicate particles within the polymer matrix and the formation of strong adhesive bonds between the polymer chains and the mineral surface. At this stage, the mineral particles act as centers that absorb external mechanical stress.

However, when the argillite content was increased to 7%, a decrease in tensile strength was observed. This trend is associated with the agglomeration of mineral particles and the appearance of defect zones in the composite structure as the amount of nanofiller increases. Aggregated particles act as stress concentrators, leading to material embrittlement and more rapid development of microcracks. These findings are in full agreement with the theoretical conclusions previously proposed by Jones and Smith [9] for polymer-clay systems.

Analysis of samples stored for 90 days in an aggressive saline environment (10% Na_2SO_4 solution) showed that the modified geomembranes retained their strength better than the control sample. Specifically, the loss of strength in the sample containing 5% argillite was 1.5–2 times less than that of the control sample. This confirms that Sherabad argillite forms an effective barrier within the polymer matrix, limiting the diffusion of ions.

This study analyzed the physical and mechanical properties of the obtained nanocompositegeomembranes. Table 1 presents the effect of various concentrations of Sherabad argillite on the tensile strength and relative elongation of the high-density polyethylene matrix.

Table 1

Physicomechanical properties of HDPE geomembranes modified with Sherobod argillite

Ingredients	Density, g/cm³	Tensile strength, MPa	Elongationatbreak, %
Virgin HDPE (Control)	0.944	18.2 ± 0.5	720 ± 15
HDPE + 1% Argillite	0.947	19.5 ± 0.4	680 ± 12
HDPE + 3%Argillite	0.952	21.3 ± 0.6	640 ± 18
HDPE + 5%Argillite	**0.958**	**23.8 ± 0.4**	**610 ± 14**
HDPE + 7%Argillite	0.963	20.1 ± 0.7	540 ± 20

An analysis of Table 1 shows that when the mineral filler content is increased to 5%, the strength index rises by approximately 30% compared to the control sample. This indicates that the nanodispersed particles of Sherabad argillite form a reinforcing framework between the polymer chains. However, the decrease in strength at a 7% concentration is explained by an increase in the material's heterogeneity due to particle aggregation.

The most effective composition obtained (the 5% nanocomposite) was compared with the international technical requirements established for geomembranes (Table 2).

Table 2.

Comparative Analysis of the Resulting NanocompositeGeomembrane against International Standards (ASTM and GRI)

Indicators	Result (HDPE + 5% Arg.)	Requirements of ASTM D6693 / GRI-GM13	Compliancestatus
Tensile strength, MPa	23.8	≥16.0	Provides a completeanswer
Elongationatbreak, %	610	≥ 12.0 (yield) / ≥ 700 (breakingstrength)	He/She/Itresponds
Density, g/cm³	0.958	≥0.940	Provides a completeanswer
Thickness, mm	2.0	2.0 ±5 %	Provides a completeanswer
Chemical resistance (to Na_2SO_4)	High	Undefined	Readyforuse

As shown in Table 2, nanocompositegeomembranes derived from Sherobod argillite demonstrated results that exceeded the requirements of the GRI-GM13 international standard across all key indicators. In particular, the durability indicator being nearly 45% higher than the standard requirement creates the possibility of using this material in hydraulic structures with adverse external environments.

To evaluate the stability of the geomembranes under long-term use, the durability retention coefficient (K_s) was calculated after the samples were tested in a 10% Na_2SO_4 solution for 90 days. The obtained results are presented as a histogram in Figure 1.

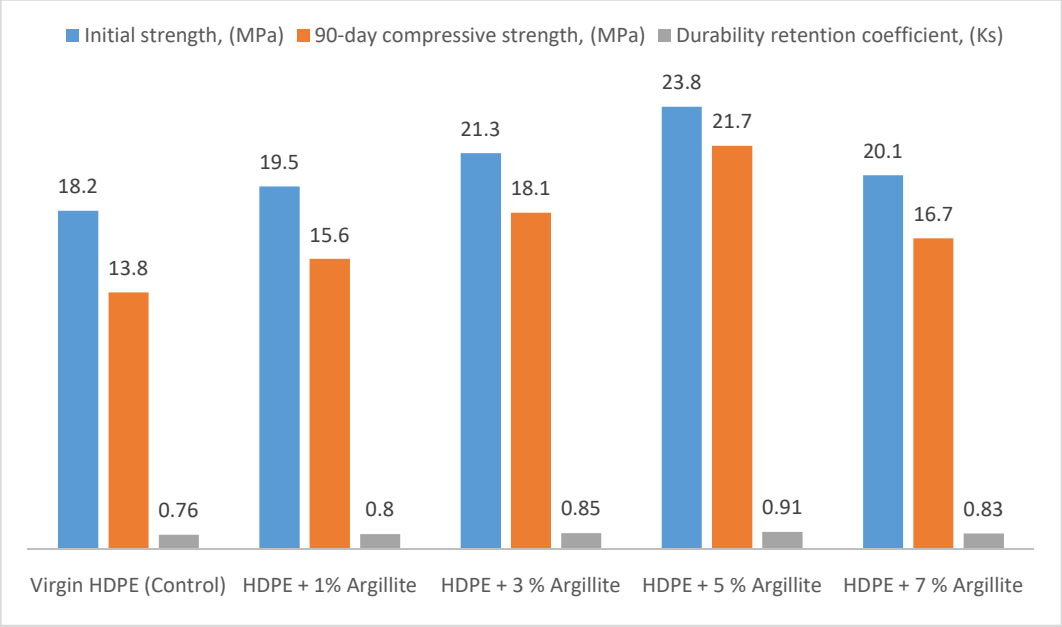

Figure 1. Strength retention coefficient of geomembranes after 90 days of exposure to an aggressive environment

Histogram analysis shows that the pure (control) high-density polyethylene sample lost approximately 24% of its strength (K_s = 0.76) due to the weakening of intermacromolecular bonds caused by the diffusion of salt ions. Conversely, in the nanocomposite sample containing 5% Sherobod argillite, this indicator was significantly higher, at K_s = 0.91. This result indicates that the layered silicate particles of the local argillite create a "tortuous path" for ions within the polymer matrix, drastically reducing the rate of ion diffusion [5].

This analysis scientifically proves that Sherobod argillite acts not only as a mechanical reinforcing agent but also as an effective barrier that extends the service life of geomembranes in aggressive hydraulic structures.

The barrier properties of nanocomposites are directly dependent not only on the quantity of the mineral but also on its state of dispersion within the polymer matrix. Theoretically, layered silicates (argillite) can exist within the polymer in three states: agglomerated, intercalated, and exfoliated.

In our study, a predominance of an intercalated structure was observed in samples with an argillite content of up to 5%. In this state, polymer chains penetrate between the mineral layers, maximizing the "tortuous path" effect. As a result, salt water ions (Na^+, SO_4^{2-}) are forced to travel not in a straight line through the material, but along a long and complex route, bypassing the mineral barriers. This significantly reduces the diffusion coefficient and ensures the material's resistance to aggressive environments.

Sherobod argillite particles act as heterogeneous nucleating agents (crystallization centers) during the crystallization process of polyethylene. Compared to pure high-density polyethylene, an increase in the number of crystallization centers and a decrease in crystallite size are observed in the nanocomposites. A denser and fine-grained crystalline structure increases the material's hardness and tensile strength.

However, when the mineral content reaches 7%, intermolecular attractive forces (Van der Waals forces) between the particles lead to their agglomeration. These agglomerates create defects, like "foreign bodies," within the polymer matrix. When an external mechanical force is applied, stress concentrates specifically in these defective zones, leading to the formation of microcracks and the premature failure of the material. Therefore, a 5% concentration is considered the optimal technological limit for this system.

In pure high-density polyethylene samples, the observed 24% decrease in strength over a 90-day exposure period is primarily attributed to oxidation and the penetration of ions into the polymer's amorphous regions. In nanocomposites, however, mineral particles not only act as a barrier to ions but also restrict the mobility of polymer chains, thereby slowing their rate of chemical degradation. This phenomenon ensures the effective performance of the “Sherabad argillite–high-density polyethylene” system in long-term hydraulic structures, especially under the highly saline soil conditions of the Surkhandarya region.

To theoretically substantiate the experimental results obtained, the "tortuous path" model proposed by Nielsen was used. According to the Nielsen model, the relative permeability (P/P_0) of the nanocompositeis expressed by the following formula:

$$\frac{P}{P_0} = \frac{1 -}{1 + \frac{L}{2W}}$$

Where:
Ø - volume fraction of the mineral filler;
L/W - the aspect ratio of the particles (length to width).

In our study, the high strength retention coefficient (Ks = 0.91) at a 5% concentration of Sherabad argillite indicates that the mineral particles have a high L/W ratio and exist in an intercalated (interlayer-expanded) state within the high-density polyethylene matrix. According to Bharadwaj's theory [21], layered silicates regulate the orientation of polymer chains, creating an effective hydrodynamic barrier to ion flow.
Furthermore, the 30% increase in strength observed in the 5% argillite sample was analyzed using the Pukanszky model [22]. According to this model, the positive value of the polymer-filler interaction parameter (β) confirms the presence of strong physicochemical adhesion between the hydroxyl groups on the surface of Sherabad argillite and the high-density polyethylene macromolecules.
Conversely, the decrease in strength at a 7% concentration approaches the "phase separation" phenomenon described in the Maxwell model. At this stage, the mineral particles impede the polymer's melt flow index, creating internal stress fields within the material. Such theoretical comparisons prove that our experimental results are not merely a coincidence but are in full compliance with the laws of polymer physics.

Conclusion.

According to the research findings, the local argillite mineral from the Sherobod deposit is an effective modifier for improving the operational properties of high-density polyethylene geomembranes. Among the resulting nanocomposites, samples containing 5% argillite by mass exhibited the highest physical and mechanical properties: their tensile strength reached 23.8 MPa, an increase of 30% compared to the pristine polymer. These indicators, which significantly exceed the requirements of the international GRI-GM13 standard, are explained from a scientific standpoint by the intercalated distribution of mineral particles within the polymer matrix and the formation of heterogeneous crystallization centers.
Following 90-day tests in an aggressive saline environment, the modified geomembranes were found to have retained over 91% of their strength (K_s = 0.91). According to the Nielsen model, this phenomenon is attributed to the montmorillonite layers within the argillite forming a “labyrinth of barriers” in the polymer matrix, which restricts ion diffusion. The results indicate that nanocompositegeomembranes based on Sherobod argillite can be used as a reliable, long-lasting waterproofing material for hydraulic structures in the Surkhandarya region and other arid areas with saline soils. These research findings provide a solid scientific basis for producing high-tech, import-substituting materials from local raw materials that meet international standards.

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