Study of Crack Resistance of Polyethylene Composite Materials

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Abstract. The article presents the study of stress intensity factor of polyethylene composite materials containing different fillers. The coefficient of the crack resistance of the materials was considered as an indicator of the low-temperature properties of composites. It has been established that to improve the crack resistance of polyethylene, the use of plasticizers is effective, provided that the fiber is well wetted with a polymer melt.

1. Introduction

The development of polymeric composite materials for use in regions with severe climatic conditions characterized by extremely low temperatures during the winter period predetermines the use of additional methods for assessing their operational properties. At low temperatures, most polymeric materials become brittle. Embrittlement occurs due to a decrease in the macromolecular mobility of polymer, which causes a decrease in the speed of relaxation processes under various mechanical impact [1]. One of the most common polymeric materials commonly used in industry and the economy in a wide range of products is polyethylene (PE). The most important products made of polyethylene are pipes used for water and gas supply in municipal engineering, as well as in almost all industries. It is possible to increase the resistance of polyethylene pipes to destruction at low temperatures in several ways. First, the most common way to protect pipes from exposure to low temperatures is to lay pipelines underground in special trenches. A feature of permafrost soils is that in winter at the depth of 1-1.5 m, their temperature does not fall below minus 15°C [2]. Thus, the laying of the pipeline underground provides the safety of pipes from freezing, and also limits the possibility of accidental mechanical effects. Second, the temperature in the pipe wall can be controlled by a continuous flow of liquid with a certain temperature, for example, water. According to this approach, the problem is solved in the system of municipal water supply. Third, it is possible to improve the frost-resistant properties of polyethylene by modifying them, i.e. developing frost-resistant polyethylene composite materials.

Assessing the low-temperature properties of polymer composites is of great interest. Such attention is determined by both intensive processes of industrial development of the Northern and Arctic regions of the Russian Federation, and an increase in the living standards of the population. Depending on the properties of the material, the destruction at negative temperatures can occur both brittle and viscous. Features of the destruction will depend on the speed and strength of the destructive effect, as well as on the state of the polymeric material product. Thus, under a slow static effect, the polymer material may either not collapse or undergo gradual plastic deformation. In the case of a sharp effect, especially
if there are microcracks in the product, the material may break in a brittle way. The first case relates to the standard material strength, which can be assessed according to the tensile strength of the polymeric material at negative temperatures. The second case relates to the special material property – its crack resistance, for the assessment of which there are various techniques.

The purpose of this work is to assess the crack resistance of polyethylene composite materials containing different fillers.

2. Objects and Research Methods
A variety of factors influences the mechanical properties of polymeric materials, including low-temperature properties: the structure of the macromolecular chains, the submolecular structure, the composition of the materials etc.

In this work, we used two grades of PE: PE80B (PE80) and PE2NT11 (PE100) produced by PJSC Kazanorgsintez. The numerical index characterizes the minimum required strength (MRS) of polyethylene pipe grades, i.e. strain, which determines the material properties used for manufacturing pipes, and obtained by extrapolation for a lifetime of 50 years at a temperature of 20°C according to the results of pipe tests to a constant internal hydrostatic pressure. The growth in MRS of modern PE grades for pipes is due to adding low-molecular comonomers — butene, hexene, etc. — into the polymerization process, which leads to the formation of low-molecular branches on polyethylene molecules. The low-molecular part of the polymer forms crystalline regions, due to which the density, short-term and long-term strength, and the elastic modulus of the material increase.

It is possible to increase the crystallinity of PE by adding nanomodifiers, which are the centers of structure formation providing a more ordered structure [3]. In this work, magnesium nanospinel (MNS) synthesized at the Institute of Solid State Chemistry and Mechanochemistry SB RAS (Novosibirsk) was used as a nanofiller (nanomodifier).

Another way to improve the low-temperature properties of polyethylene is plasticization. Based on the analysis of the plasticizer properties and the characteristics of their effect on the mechanical properties of polymers at low temperatures, we chose three plasticizing additives: stearic acid (SA, GOST 6484-96 (State Standard)), dibutyl sebacate (DBS, GOST 8728-88 (State Standard)) and dioctyl terephthalate (DOT, TU 2493-003-641238436-2013 (specifications)). These substances reduce friction between the macromolecules of the polymer during deformation, which leads to an increase in the material elasticity even at low temperatures [4-6].

The third method improving the crack resistance of polyethylene composite materials is disperse reinforcement. The chopped carbon fibers were added into the polymer because of the assumption that short fibers could prevent the spread of a crack due to covering the crack mouth. Carbon fibers of two grades were used as reinforcing additives: UVIS-AC-P (fibrous material based on cellulose hydrate) and UKN-M (fibrous material based on polyacrylonitrile) produced by Uvicom Co Ltd. The chosen fillers were chopped with the length of 6-7 mm and the diameter of 5-8 microns.

The crack resistance of materials, as a criterion of low-temperature properties of polyethylene composites, was assessed according to the method described in [7] at the temperature of minus 15°C and at the speed of the tensile machine traverse of 500 mm/min.

3. Results and Discussion
The stress concentrator in the construction of plastic pipelines are welded joints [8, 9]. Often, violations in the welding technology, such as overheating of the material, offset of the center of welding, contamination of the ends of the welded pipes can lead to microcracks in the material. Therefore, to assess the crack resistance of polyethylene and nanocomposites, we consider both the crack resistance of the bulk material and the welded butt joint. Table 1 presents the study of the stress intensity factor $K_{IC}$ (one of the crack resistance indicators) of the bulk material and welded joints of nanocomposites based on PE80B.
Table 1. Crack resistance of the bulk material and the welded butt joint of nanocomposites based on PE80B.

| Composition                          | $K_{1C}$ [MPa/m$^{1/2}$] (bulk material) | $K_{1C}$ [MPa/m$^{1/2}$] (welded butt joint) |
|--------------------------------------|----------------------------------------|-----------------------------------------------|
| PE80B                                | 5.43±0.49                              | 3.98±0.67                                     |
| PE80B + 0.05 wt.% MgAl$_2$O$_4$       | 5.42±0.48                              | 3.70±0.25                                     |
| PE80B + 0.1 wt.% MgAl$_2$O$_4$        | 5.62±0.25                              | 3.33±0.41                                     |
| PE80B + 0.5 wt.% MgAl$_2$O$_4$        | 4.52±0.24                              | -                                             |
| PE80B + 1.0 wt.% MgAl$_2$O$_4$        | 4.45±0.14                              | 3.04±0.28                                     |
| PE80B + 2.0 wt.% MgAl$_2$O$_4$        | 4.20±0.18                              | 3.11±0.22                                     |

The research results show that the crack resistance of low-filled nanocomposites almost does not differ from the crack resistance of the original PE. With an increase in the concentration of magnesium spinel, the crack resistance of the bulk material gradually decreases. The values of $K_{1C}$ in welded butt joints are significantly lower than in the bulk material. Thus, it is shown that the addition of nanofillers leads to an increase in defects of the material and a decrease in the material resistance to crack propagation. Welding, as a process causing defects, in combination with nanomodification also contributes to a decrease in the crack resistance of the material and can lead to the destruction of the pipeline in the welded under high external or internal stresses. Thus, nanomodification as a way to increase the crack resistance of the material should be considered ineffective.

As mentioned above, plasticization is one of the effective ways to increase the crack resistance of polymeric materials. Table 2 presents the study plasticized polymer composite materials based on PE2NT11.

Table 2. Crack resistance of plasticized polyethylene composite materials.

| Composition       | $K_{1C}$ [MPa/m$^{1/2}$] (bulk material) |
|-------------------|----------------------------------------|
| PE2NT11           | 14.89±0.53                             |
| PE2NT11 + 3.0 wt.% DBS | 16.46±0.36                           |
| PE2NT11 + 3.0 wt.% DOT | 14.24±0.37                           |
| PE2NT11 + 3.0 wt.% SA       | 17.53±0.28                             |

It can be seen that the crack resistance of polyethylene composites depends on the chemical structure of the plasticizer. Stearic acid shows the greatest efficiency. However, the observations of the surface of the composite containing this plasticizer showed that the surface of the sample gradually becomes hazy. This indicates a poor solubility of stearic acid in polyethylene. Consequently, its use should be considered inexpedient. Thus, the most effective plasticizer from the considered ones is DBS. It should be noted that it is not possible to compare the indicators of the crack resistance of the materials presented in Table 1 and 2, as the samples with different geometric parameters were used in the study. Despite the fact that the crack resistance is a constant for any material [10], in order to compare these parameters, studies should be carried out in strictly identical conditions.

Table 3 shows the study of the stress intensity factor of dispersion-reinforced composites based on polyethylene of grade PE80B.

Table 3. The stress intensity factor of dispersion-reinforced composites based on PE80B.

| Material                | $K_{IC}$ [MPa/m$^{1/2}$] |
|-------------------------|--------------------------|
| PE80B                   | 5.43±0.49                |
| PE80B + 10.0 wt.% UVIS-AC-P | 4.74±0.37               |
| PE80B + 10.0 wt.% UKN-M  | 6.16±0.25                |
It has been found that the value of the crack resistance of dispersion-reinforced composites is determined by the chemical nature of the initial material, from which the fiber is produced. Hence, adding 10 wt.% UVIS-AC-P fiber (the initial material is cellulose hydrate) reduces $K_{IC}$ by 13%, and the composite containing 10% wt. UKN-M fiber (the initial material is polyacrylonitrile) is characterized by 13% higher stress intensity factor compared to with unreinforced polyethylene. It is likely that the cause of the different effects of carbon fibers on the crack resistance are the features of wetting the surface of the fibers during the processing of composites into products. Since the fibers are made of different initial materials, the set of residual ions can predetermine the hydrophilicity or hydrophobicity of their surface.

4. Conclusion

Thus, studies of the crack resistance of polyethylene composites containing different fillers showed that adding nanofillers is an ineffective way to improve this characteristic. The effectiveness of plasticizing additives is determined by their chemical nature and depends, probably, on the ability of the additive to dissolve in the polymer matrix. Chopped carbon fibers also ambiguously affect the $K_{IC}$ material, which is determined by the wettability of the fiber surface with the polymer binder: the better the wetting, the higher the crack resistance.

5. References

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