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On the Causes of Defects in the Welded Joints of Pipes Made of PE100

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Abstract—Pipes with the defects of the welded joint (cavities, inclusions, brittle fracture) are studied, and their relationship with the characteristics of the feedstock is shown. Qualitative and quantitative indicators of the concentration of volatile substances of various fractions in the granules of polyethylene are obtained. The value of moisture absorption of carbon black concentrates used in the production of PE100 is determined.

Keywords: polyethylene 100, defects of the welded joint, type of carbon black, volatile compounds, gas chromatography—mass spectrometry

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INTRODUCTION

Water pipes made of polymers and their compounds have almost completely replaced pipes made of concrete and metal in the market. The application of plastic pipes for water main offers significant advantages, determined by their properties such as the relative simplicity of assemblage, possibility of duct-free plumbing, durability, and low cost [1].

PE100 is a reliable piping material that differs from other large-tonnage thermoplastics by its excellent chemical resistance, strong resistance to thermooxidative destruction, and stability of properties in time. Indeed, these advantages are maintained under the condition of the conformance of the feedstock with state standard (*GOST* (State Standard) *18599-2001* and *GOST* (State Standard) *50838-2009*). The violation of the parameters of production and processing of PE100 results in a change in the macromolecular structure of the polymer and its physical properties and performance indicators. The capacity of pipes for defect-free welding between each other belongs to one such indicator.

The process of welding (we considered hot tool butt welding [2]) is executed upon the assemblage of pipes and should be performed in strict adherence with the established standards (*GOST R 55276-2012*). However, even strict adherence to all the regulated parameters does not always guarantee the high quality of a welded joint.

EXPERIMENTAL

The aim of this work is to study the properties of different lots of PE100 of a serial brand and their influence on the quality of the welded joints. Pipe products fabricated from this brand of PE100 sometimes have faults that lead to a significant decrease in the physicochemical characteristics and the impossibility of welding. Various defects (pores, regions of faulty fusion, inclusions) were recorded on the surface of the welded joint upon welding (Fig. 1). In addition, as shown by the tests, the welded joint underwent brittle rather than plastic fracture.

MATERIALS AND METHODS

1. Determination of the weight fraction of volatile substances according to *GOST 26350-84*.
2. Determination of the weight fraction of volatile substances at 105°C using an HR83 halogen moisture analyzer (Mettler Toledo).
3. Determination of the weight fraction of water by coulometric titration.
4. Determination of the dynamics of moisture absorption of CBCs.
5. Determination of the qualitative composition of the volatile compounds released upon heating the samples by gas chromatography—mass spectrometry.
6. Fourier-transform IR spectroscopy (the IR spectra were recorded in the ATR mode using a diamond crystal at a resolution of 2 and a spectral range of 4000 to 400 cm^{-1} on a Nicolet iS50 FT-IR instrument (Thermo Scientific)).

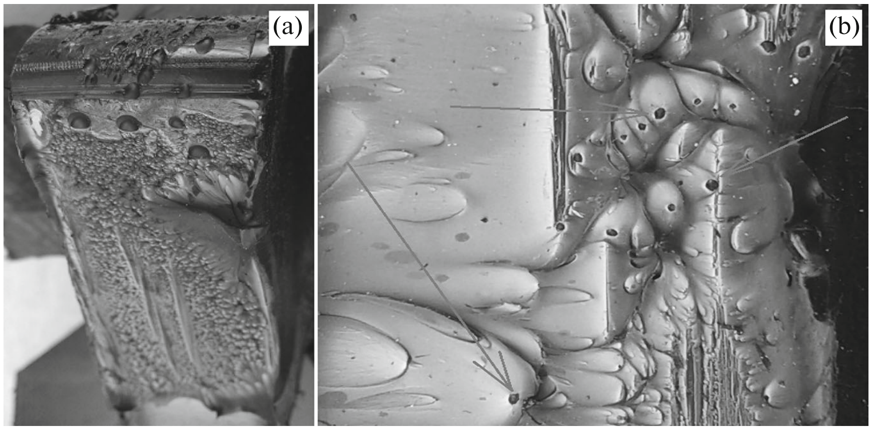

Fig. 1. Examples of off-grade welded joints (cavities and zones of faulty fusion are seen; the arrows on the right show the inclusions of the agglomerates of carbon black).

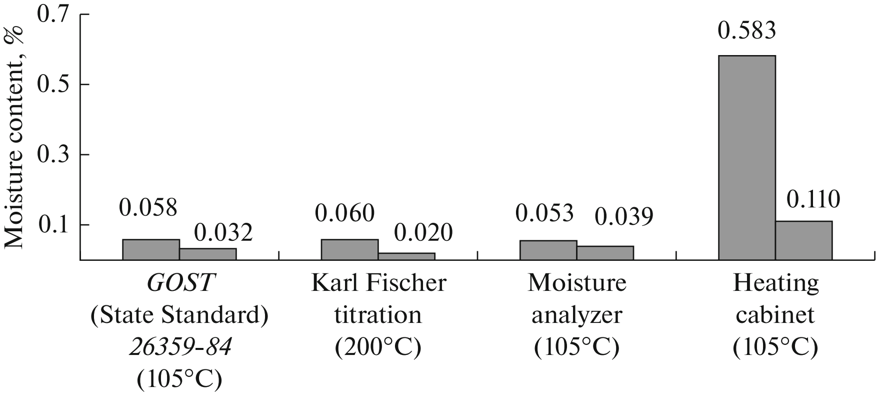

Fig. 2. Histogram of moisture content in lot A (left) and lot B (right).

7. Scanning electron microscopy (a Phenom ProX instrument (Phenom-World); the accelerating potential of 10–15 kV, a backscatter electron detector).

8. Optical microscopy in transmitted and incident light using (or without using) ordinary polarization (an Eclipse LV100 instrument (Nikon)).

RESULTS AND DISCUSSION

One of the reasons for the formation of cavities on the surface of a welded joint can be an increased concentration of moisture and low-boiling compounds in the lots of PE under study. The deterioration of this indicator can lead to the intolerable drop in the quality of the welded joint because the release of volatile compounds in the process of welding induces the formation of bubbles and bumps [3]. To refine this hypothesis, we performed the set of studies presented below.

In industry, a parameter such as the concentration of volatile substances is controlled (not more than 0.035%) and is measured according to *GOST 26350-84*. To rectify and confirm the obtained results, additional analyses are performed, including Karl Fischer coulometric titration and a measurement on a halogen moisture analyzer. These methods allow determining only the concentration of water because they are conducted at 105°C.

To detect other low-boiling compounds in the polymer, a measurement in a heating cabinet at 230°C (the maximum temperature mode of welding) was used. Two lots of polyethylene pipes, A and B, were compared. The formation of defects on the welded joint is characteristic for the pipes from lot A and is not characteristic for the pipes from lot B.

The results of all the studies are fully correlated with each other (Fig. 2) and indicate an increased concentration of water and other low-boiling volatile compounds in lot A compared to lot B.

Based on these results, it was decided to analyze the moisture absorption of the carbon black concentrate used in this brand of PE100 (the ISAF type of carbon black, the concentration is 40%) because carbon black belongs to hygroscopic materials. The ability of CBCs to absorb moisture directly depends on the particle size and presence of impurities. The amount of absorbed moisture is also affected by the sorption capacity and storage conditions of CBCs [4]. There are currently several types of carbon black used in CBCs, namely, ISAF, HAF, FEF, SRF, and P-type. Concentrates containing high-structure types of carbon black with a large specific surface area (ISAF, HAF) possess excellent tinting power and maximum opacity; however, these types of carbon black can only be finely dispersed in the case of their concentration in the concentrate of not more than 40%. Carbon blacks of the P-type belong to the extra pure grade and are intended for the tinting and light stabilization of plastics, especially polymer compounds for stand-pipes (gas and water). Their difference mainly consists in the fact that they have a very low (less than 0.1%) concentration of ash, sulfur, and extractables. Because of this, this brand is authorized for use in the goods in contact with food products and water supply pipes. Linear low-density polyethylene possessing good wetting and dispersing properties serves as the polymer base [5]. A CBC containing carbon black of the P-type at a concentration of 40% was chosen for comparison with the sample under study.

Experimental conditions: the preliminarily dried samples with a weight of 10 g were immersed into a desiccator, onto the bottom of which a bowl of water was placed. The concentration of moisture was measured every week by the increase in the weight of the samples. The duration of the experiment was 10 weeks.

It can be concluded based on the performed study that the final value of moisture absorption in the studied samples differs by a factor of 1.75 (0.69% in the CBC based on the P-type carbon black versus 1.21% in the CBC based on the ISAF carbon black) (Fig. 3).

To perform the qualitative and quantitative determination of the volatile compounds released upon heating, the granules of PE were analyzed by GC–MS. Experimental conditions: (1) the samples were heated at 200°C for 40 min followed by the analysis by GC–MS using a TriPlus RSH headspace autosampler and (2) the samples were heated in a heating cabinet at 300°C for 20 or 30 min and analyzed by GC–MS using a headspace autosampler. The results are presented in Tables 1 and 2.

The results of the study give indicate a greater number of volatile compounds in lot A (25) compared to lot B (4). This can result from the violation of the process parameters of the synthesis of the polymer (in particular, the concentration of impurities in the initial monomers can differ). In addition, the volume of the volatile compounds released at 190–210°C from the sample from lot A is quadruple the similar indicator for lot B (58.59 versus 14.05%). This explains the formation of bubbles on the welding surface of the pipes as a result of the migration of the high-boiling fraction from the bulk of PE100 in the melt.

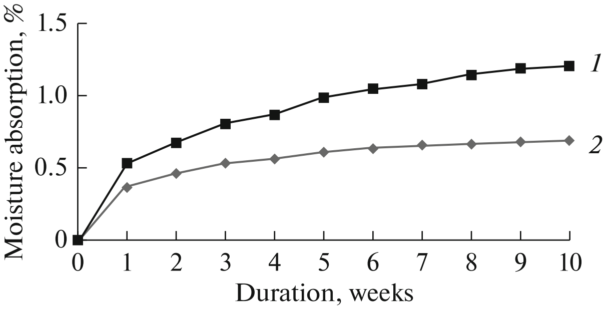

Fig. 3. Dynamics of the moisture absorption of CBCs.

To determine the amount and composition of the volatile compounds in the temperature range of 200–400°C, the use of an EGA/PY-3030D accessory for pyrolysis GC–MS was analyzed. The results showed that the samples from lot A had an increased concentration of C_{16} to C_{36} hydrocarbons (16.8%) in comparison with the samples from lot B (9.1%). This can also result from the violation of the process parameters at the stage of the synthesis of the polymer.

To measure the welded joint efficiency, bending tests of the blades from the welded joints (pipes from lot A) were performed. The welding occurred at a high pressure and $T = 200$–210°C. The fracture of the sample occurred under bending making an angle of ~25°. A strongly pronounced brittle fracture and local regions of faulty fusion resembling stripes with a width of up to 4 mm orientated from the center of the wall of the pipe to the external and internal surfaces were observed.

We isolated and analyzed the following regions on the surface: (1) the fracture plane was smooth, (2) the fracture plane was bubbly, (3) stripes of faulty fusion, and (4) body of the pipe. According to the data of Fourier-transform IR spectroscopy (ATR), the IR spectra of all the studied regions correspond to the spectrum of polyethylene. The thermal stability (IPO) in all the deformed segments was more than 90 min at 200°C.

The fracture plane was studied by optical and scanning electron microscopy. Dark regions, the so-called crosses, appear in the image in polarized light (Fig. 4a). Spherulites and supramolecular crystalline buildups, generally appear the same in the case of the study of polymers in polarized light. The initial lamella growing from the primary nucleus branches out into the defective points (dislocations) of the crystal lattice to form secondary lamellae that bend and intertwine as they grow and then also branch out to form tertiary lamellae, etc. Eventually, many fibrous lamellae are formed that diverge in all the directions radially from the center until their growth is stopped as a result of the neighboring spherulites piling onto each other [6]. This process is to a great extent determined by the rate of crystallization of the material. The lower the rate of the process of crystallization (rate of cooling) the

Table 1. Qualitative and quantitative composition of the volatile compounds released upon heating the samples from lots A and B

Retention time, min	Substance	Boiling point, °C	Peak area, %	
			lot A	lot B
1.08	Heptane	98.4	10.5	–
1.71	2-Hexanone	128	7.38	3.15
1.76	Octane	125.7	5.18	–
5.83	4-Octanone	172–174	1.35	
6.28	Decene	170.6	5	
6.37	2-Octanone	172–174	4.47	
6.52	Decane	174	9.93	10.9
6.68	Octanal	163.4	4.93	–
8.34	Dibutyl ketone	181–187	1.41	
8.76	Heptyl methyl ketone	181–187	2.21	
8.83	Undecane	195.9	3.05	
8.97	Nonanal	190–192	3.18	
10.48	Dodecene	213.4	0.75	
10.62	Dodecane	216.3	12.19	80.03
10.76	Decanal	208–209	1.01	–
12.14	Tridecane	235.5	1.04	
12.31	Undecanal	223	0.51	
13.41	Tetradecene	251.1	0.32	
13.51	Tetradecane	253.6	12.36	5.91
13.70	Dodecanal	249	0.27	–
14.77	Pentadecane	270.6	0.42	
15.95	Hexadecane	286.8	5.56	
17.07	Heptadecane	301.9	0.37	
18.13	Octadecane	316.1	5.65	
20.10	Icosane	342.7	0.94	

larger the size of the spherulites. Individual regions in the form of polygons are clearly seen (Fig. 4b). Attention should be paid to the structure of the surface of each of the polygons; thus, the center from which the rays stretch in the radial direction is clearly seen in each of them. In our opinion, such a structure confirms the results of optical microscopy in polarized light and makes it possible to assume that the observed polygons are quite large (with a diameter of 300 to 400 μm) polymer spherulites. Optical microscopy of the surface of the welded joint showed that the presence of the agglomerates of carbon black found in the material of the off-grade welded joint was another of the possible reasons leading to the internal defects of the welded joint (Fig. 4c).

Table 2. Approximate assay of volatile compounds released upon heating the samples (with respect to the fractions with different boiling points)

Sample	Assay, %		
	$T_b < 110°C$	$110°C < T_b < 220°C$	$T_b > 220°C$
Lot A	10.5	62.0	27.5
Lot B	3.15	90.93	5.91

Probably, regions of point overheating appear in the process of welding the pipes, in which gaseous compounds released from the material are accumulated. As a result of this, cavities (bubbles) are formed in the local regions of the welded joint, the walls of which are formed by large spherulites of the polymer.

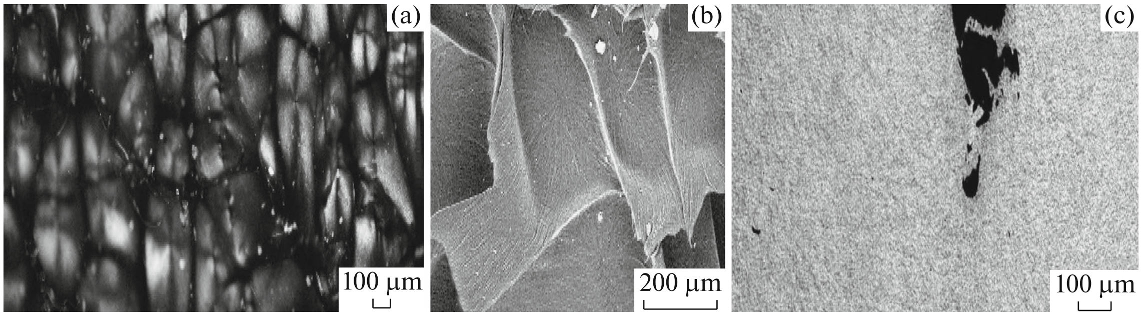

Fig. 4. The fracture plane is bubbly: (a) optical microscopy, incident light, ordinary polarization, (b) SEM (compositional mode), and (c) micrographs of the samples of the films fabricated from PE from lot A obtained from blades in transmitted light.

The spherulites are strongly formed, while the space between the spherulites is a stressed region with reduced strength. Because of this, the fracture of the joint in the bubbly region occurs around the spherulites. Spherulites are also present in the smooth region of the fracture plane; however, they have a significantly (by dozens of factors) smaller size compared to the bubbly region, and the space between the small spherulites is less stressed.

CONCLUSIONS

The study of an array of samples of PE from different lots (granulate, pipes, welded joints) made it possible to find the three main problems that are most often encountered in the case of the use of this feedstock.

The first problem is the nonuniform distribution of carbon black in the polymer matrix, which leads to the formation of large agglomerates that act as stress concentrators. Brittle fracture is observed as a result, more often in the body of the pipe but sometimes (locally) along the welded joint.

The second problem is also directly associated with the quality of CBCs. The use of cheap brands of CBCs based on carbon blacks with high sorption capacity leads to the fact that the moisture content in the material becomes above the standard (0.035 wt %), and the pipe acquires porosity; this is especially manifested on the burr of the welded joint.

The third problem is the presence of a large number of volatile compounds with the boiling point in a range characteristic for the process of processing of this feedstock in the material. The presence of such fractions can lead to the appearance of defects in the form of pores or cavities formed in the products in the process of their fabrication as well as induce the deterioration of the quality of the welded joint during the welding of finished products. This type of impurities cannot be removed using standard dryers. It is only possible to distill off the high-boiling fraction from the melt. Standard pipe lines do not have degassing zones, because of which the unremoved high-boiling fraction manifests itself in the form of a bubbly surface on the welded joints, which can lead to faulty fusion.

To prevent the appearance of all the above defects in finished products, it is necessary to perform thorough incoming control of the purchased feedstock and rejection of the off-grade material. The concentration of moisture and other volatile compounds and moisture absorption should be more thoroughly analyzed, and the type of carbon black used in the polyethylene compound should be determined. The nonconformance of these parameters with the established and recommended standards can lead to the appearance of defects of welded joints.

ABBREVIATIONS

PE100	polyethylene 100
CBC	carbon black concentrate
ATR	attenuated total reflection
ISAF	intermediate super abrasion furnace
HAF	high abrasion furnace
FEF	fast extrusion furnace
SRF	semi-reinforcing furnace
GC—MS	gas chromatography—mass spectrometry
IPO	induction period of oxidation
SEM	scanning electron microscopy

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

SUPPLEMENTARY MATERIALS

There are no supplementary materials.

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