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Main Limiting Parameters of Pro-oxidant Additive Production and Processing

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Abstract

The article discusses technological behaviour of pro-oxidant additives – PVD 15803-020 low density polyethylene (LDPE) with a variable-valence metal (cobalt, copper or iron) stearate content of 5.0 and 10.0 % by mass. Limiting parameters of pro-oxidant additive production and processing were identified. Thus, thermal exposure time of pro-oxidant additive production and processing at 190 ºC is 10 minutes maximum for additives with iron stearate content of 10 % by mass and 5 minutes maximum for additives containing cobalt or copper stearate.

Keywords: PVD 15803-020 low density polyethylene (LDPE); variable-valence metal stearates; biodegradable materials; flow curves; thermal exposure.

INTRODUCTION

Development of biodegradable materials produced by modification of synthetic polymers with target additives allows making the polymers part of the natural cycles due to introduction of pro-oxidants, which demonstrate their destructive ability even in small quantities when polymers are exposed to external factors [1, 2].

Making polyolephins part of the natural environment cycles becomes possible after destruction processes when their molecular mass reaches 5000 and lower, i.e. when the polymer fragments acquire biodegradability [3], and variable-valence metal carboxylates are recommended to be used as an oxo-biodegradable additive – pro-oxidant.

In order to reduce the environmental impact, it is expedient to use biodegradable synthetic films with an iron carboxylate additive [4].

It is expedient to produce and process target additives, which are a polymer matrix containing pro-oxidants in the form of variable-valence metal carboxylates, by extrusion equipment.

However, during extrusion processing of polyolephins, changes in their molecular mass distribution were observed, while, depending on the exposure parameters, both mechanical and thermal destruction can predominate and under air oxygen, thermal oxidative destruction is observed [5, 6, 7].

It is worth noting that thermoplastics and polymer compositions are processed in extrusion equipment at high temperatures and critical shear stresses, while the presence of catalytic compounds in the form of variable-valence metal carboxylates complicates and in some cases makes it impossible to use it due to the structural transformations in the additive polymer matrix.

The research objective was to identify by capillary viscosimetry the threshold values of parameters ensuring stable thermal and thermomechanical resistance during processing of polymer matrix of pro-oxidant additives, comprising variable-valence metal stearates, in high-speed extrusion equipment.

MATERIALS AND METHODS

PVD 15803-020 low density polyethylene (LDPE), GOST 16337-77 (international standard high-pressure polyethylene (specifications) was used as a polymer base to produce pro-oxidant additives.

Variable-valence metal stearates – iron stearate TU 6-09-3738-74, copper stearate or cobalt stearate TU-2494-02-53904859-01.

SMARTRHEO 1000 capillary rheometer by Ceast with CeastVIEW 5.94 4D software and capillary diameter of 1.0 mm, lengths of 5.0 and 30.0 mm.

Prototypes of polymer additives were produced by blending in a centrifugal paddle mixer. The composition comprising PVD 15803-020 and the relevant additive (metal stearate) was fed into the hopper of a twin-screw extruder; at the die, a twill wire mesh with the mesh size of 0.4 mm and wire diameter of 0.25 mm was installed for better homogenization. The speed of extruder screws was set at 350 to 400 rpm, when the feeder was batching – at 400 to 450 rpm.

Thermostability and thermomechanical resistance of pro-oxidant additives were studied during deformation in the round channel in the shear rate range from *100* to *300* sec^{-1} with increments of *50* sec^{-1} at the temperatures from *130* to *230 °C*.

The pressure measurement error in these tests did not exceed 0.1 bar.

RESULTS AND DISCUSSION

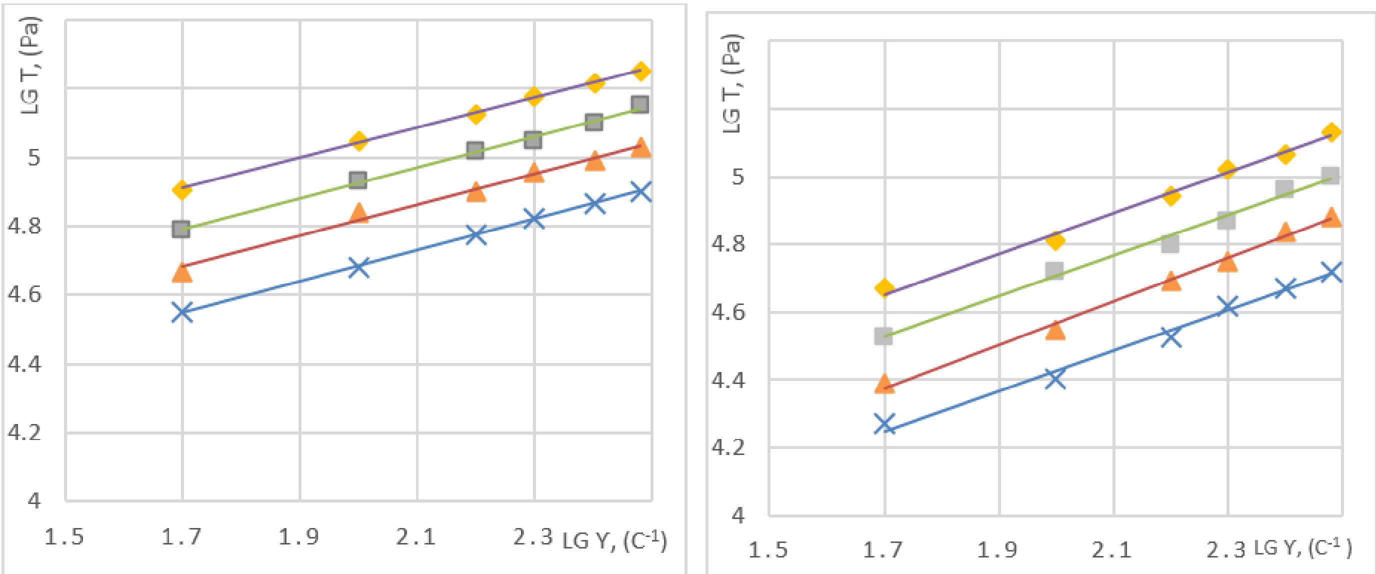
Production and processing of target additives in high-speed extrusion equipment require identification of limiting parameters ensuring stability of the additive polymer matrix structure under thermal and thermomechanical exposure in inert atmosphere in the presence of pro-oxidants – variable-valence metal carboxylates having catalytic activity. It is worth noting that the advantage of extrusion equipment is a short thermomechanical exposure of about 2.0 ÷ 3.0 minutes in the absence of oxidative medium and agents.

Reference [8] showed that it was expedient to study consequences of destructive processes in polymers under thermal and thermomechanical exposure in inert gases and air medium using a capillary rheometer that enables creating high shear stresses comparable with those developed in high-speed equipment.

Critical parameters of processing target additives with pro-oxidants in extrusion equipment lead to degradation of the additive polymer matrix thermal stability and "unstable flow" conditions resulting in distortion of extrudate surface while flowing through the tool forming channel.

Analysis of the results of pro-oxidant additive polymer matrix selection showed that it is expedient to use commercial PVD 15803-020 as a base. Justification of selecting the polymer base for pro-oxidant additive on the basis of the melt flow index parameter using IIRT-50 instrument as per GOST 11645-73 requirements is given in the reference [9].

Figures 1a and 1b show shear stresses as a function of shear rates in the temperature range from 130 to 190 °C and the shear rate range from 100 to 250 sec^{-1} for pro-oxidant additive containing 5.0% of cobalt stearate when flowing through capillaries with a diameter d = 1.0 mm and lengths l = 5.0 mm and l = 30.0 mm, respectively.



a) b)

Figure 1: Flow curves of pro-oxidant additive, containing 5.0 % by mass of cobalt stearate, through capillaries with a diameter d = 1 mm, lengths: a) l = 5 mm and b) l = 30 mm at a temperature of:

T=190˚C T=170˚C T=150˚C T=130˚C

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When the pro-oxidant additive is deformed through the capillaries, a linear relation of flow curves in double logarithmic coordinates in the investigated speed and temperature ranges is observed. With temperature increase, the functions of shear stress vs. shear rate decrease synchronously, i.e. in double logarithmic coordinates, complete invariance of flow curves with respect to the geometric parameters of the capillary is observed.

And during flowing through a 30 mm long capillary, a decrease in the shear stress values was observed, which agrees with the theoretical estimation of the macrochain behaviour when formed in a longer forming tool. When flowing, particularly in the laminar manner, the chain is straightening and the coupled or overlapped portions become smaller, i.e. orientation effects ensuring decrease in interlayer friction are observed [10].

When rheological behaviour of target additives in the temperature range from 130 to 190 °C and shear rate range from 100 to 250 sec^{-1} was studied, they were found to demonstrate stable flow when the content of pro-oxidants – variable-valence metal stearates – was 5.0% by mass. Stable flow conditions resulted in a smooth surface and uniform colour of extrudate and slight changes in its diameter. An increase in the additive retention time in the rheometer from 10 minutes to 15 minutes had no significant effect on the trend of flow curves.

However, when the pro-oxidant additives containing 10% by mass of variable-valence metals are deformed, stable flow is observed only in a limited temperature range from 170 to 190 °C. An increase in temperature above 190 °C is accompanied by the destruction of metal stearates, thus contributing to structural transformations in the additive polymer matrix, and also by gas release. As a result, the colour changes and the surface colour non-uniformity are observed.

In the photos (see Figures 2 and 3) one can see that the shape and colour of extrudate for pro-oxidant additives containing 10% by mass of cobalt stearate vary due to its high catalytic activity during structural transformations in the polymer matrix. In the course of studying the effect of temperature during pro-oxidant additive thermomechanical exposure, gas release was observed, with its intensity dramatically increasing above 200 °C. It should be noted that when a polymer matrix without any pro-oxidants was deformed, no gas release was observed up to 230 °C.

When the pro-oxidant additive containing cobalt stearate is deformed at a constant speed of 100 sec^{-1} in the capillary with a length l = 30 mm, a lighter surface with a large number of entrapped gas bubbles is observed indicating a higher intensity of structural transformations in the additive polymer matrix due to the development of higher shear stresses.

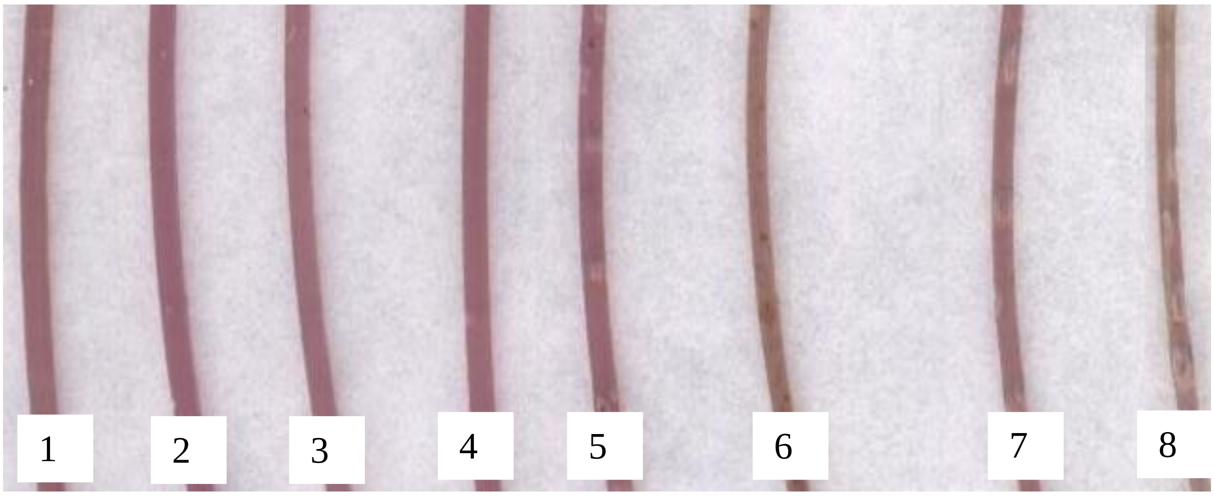


Figure 2: Photos of pro-oxidant additive extrudates containing 10% by mass of cobalt stearate when flowing through a capillary with a diameter d = 1 mm and length l = 5 mm in the temperature range, °C:

1 – 160; 2 – 170; 3 – 180; 4 – 190; 5 – 200; 6 – 210; 7 –220; and 8- 230

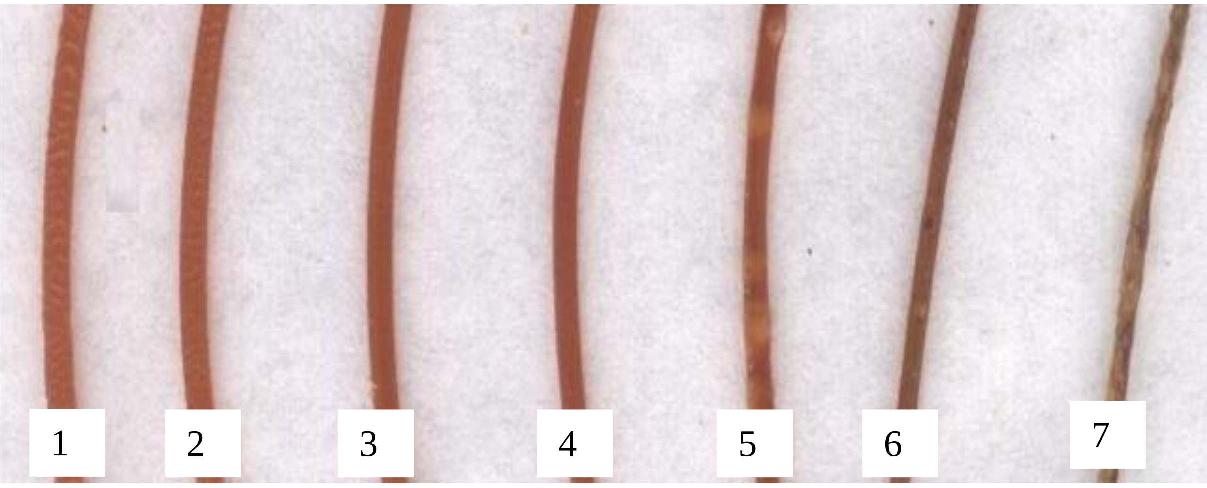
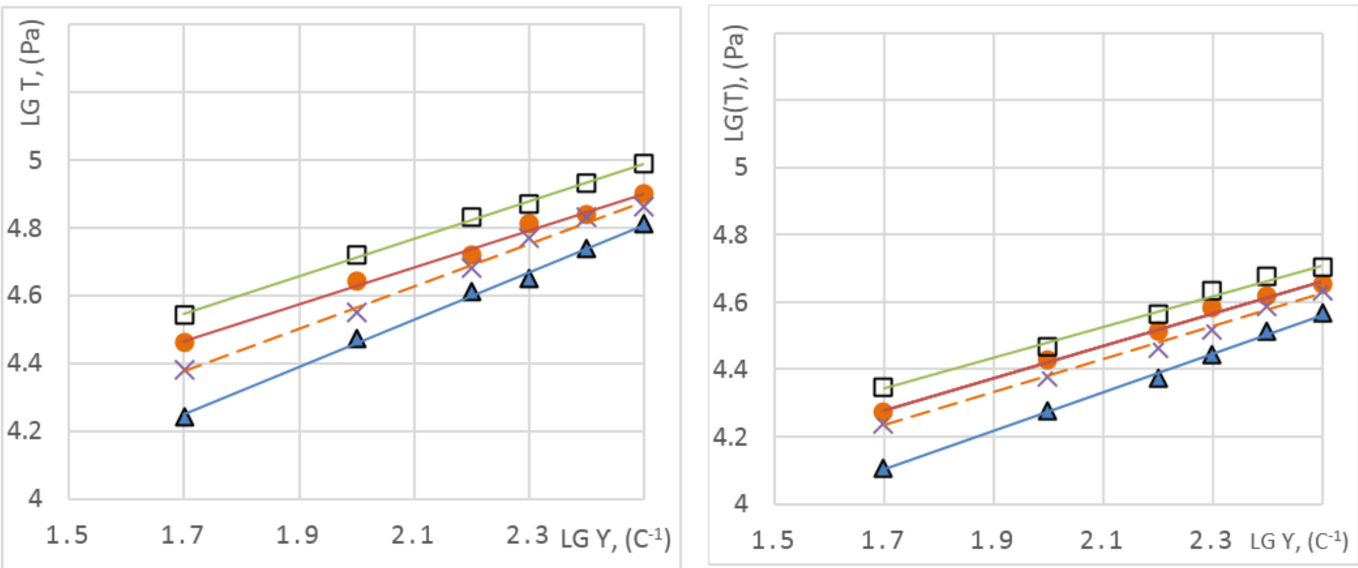


Figure 3: Photos of pro-oxidant additive extrudates containing 10% by mass of cobalt stearate when flowing through a capillary with a diameter d = 1 mm and length l = 30 mm in the temperature range, °C:

1 – 160; 2 – 170; 3 – 180; 4 – 190; 5 – 200; 6 – 210; and 7 –220.

It is evident from the curves (see Figures 4a and 4b) that when pro-oxidant additives, containing 10.0% by mass of variable-valence metals, were deformed through the capillaries a linear dependence of the flow curves in double logarithmic coordinates was observed in the investigated speed and temperature ranges. However, emphasis should be laid on a more significant change in the slope of flow curves and their relative location during deformation of pro-oxidant additives containing variable-valence metals through the capillary with a length l =5 mm.



a) (T = 190˚ C, capillary 5 mm) b) (T = 190˚ C, capillary. 30 mm)

Figure 4: The change in the shear stress as a function of shear rate during deformation in the capillary with a diameter d = 1 mm with a length l = 5 mm and l = 30 mm of a pro-oxidant additive made using variable-valence metal stearates: ▲- iron stearate; ×- copper stearate; ● - cobalt stearate; □ - commercial PVD 15803-020.

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Deformation of pro-oxidant additives through the capillary with a length l =30 mm at the temperature of 190 °C is accompanied by a change in the slope of the flow curves and also by deeper structural transformations as when they are forced through the capillary with a length l =30 mm the total pressure increases several times as compared to the short capillary l =5 mm, which is illustrated in Fig. 5.

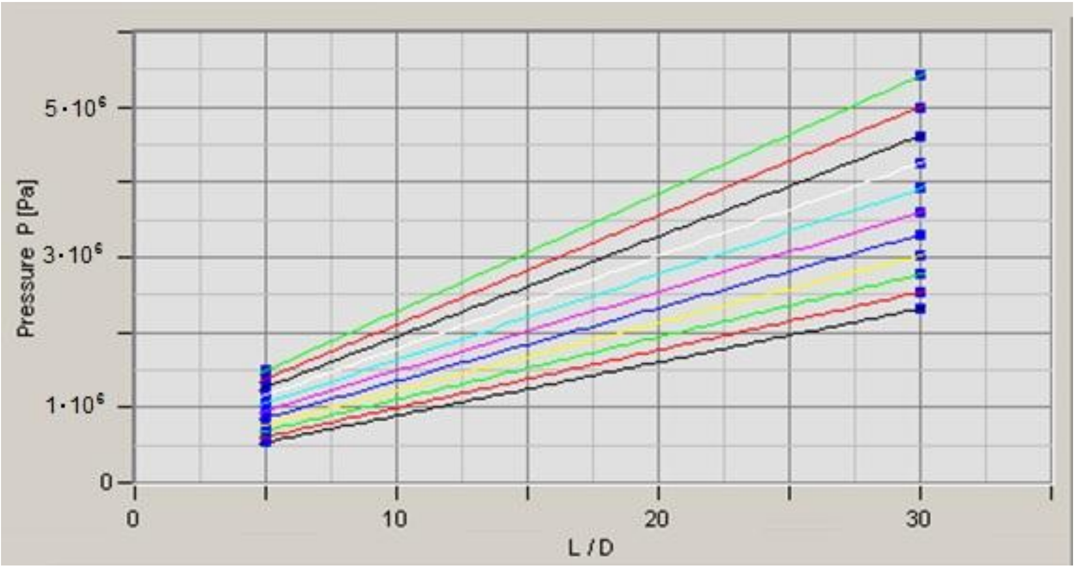


Figure 5: Pressure values before the forming tool extrapolated to the zero chamber length for PVD 15803-020 with a cobalt stearate content of 10% by mass.

However, when the polymer compositions are deformed through long capillaries, the residence time in the channel resulting in the polymer chain relaxation accompanied by a decrease in the shear stress and slope of flow curves should be taken into account.

As is evident from the analysis of flow curve trends (Figures 4a and b), the highest shear stress value was observed for the additive containing cobalt stearate, with the values decreasing in the following order: cobalt stearate>copper stearate>iron stearate.

Table 1 shows changes of pressure in the capillary and swell ratio for the extrudate of pro-oxidant additive containing 10% by mass of variable-valence metal stearates vs. those of pure PVD 15803-020, i.e. initial polymer matrix, in the temperature range from 160 to 230°C. An increase in the pressure in the capillary promotes the development of shear stresses leading to more significant structural transformations in the polymer matrix of the additive and, as a consequence, to a change in the extrudate swell ratio.

Table 1: The effect of temperature on pressurization /denominator/ and on the change in the extrudate swell ratio /numerator/ during deformation of commercial PVD 15803-020 and pro-oxidant additives on the basis thereof containing 10 % by mass of variable-valence metal stearates through the capillary (*d = 1 mm; l = 30 mm)* at a shear rate of 100 sec-^{1}

Name of material	Temperature during deformation of pro-oxidant additive through the capillary						
	160	170	180	190	200	210	230
15803-020 polyethylene	*1.22* / *5.85*	*1.25* / *5.10*	*1.22* / *4.42*	*1.20* / *3.5*	*1.17* / *3.8*	*1.11* / *3.2*	*1.01* / *2.56*
Additive containing iron stearate	1.38 / 3.10	1.37 / 3.15	1.25 / 2.60	1.15 / 1.90	1.08 / 1.70	0.92 / 1.60	0.79 / 1.50
Additive containing cobalt stearate	1.14 / 5.50	1.15 / 5.30	1.21 / 5.2	1.22 / 4.5	1.12 / 4.3	1.05 / 4.2	0.81 / 3.8
Additive containing copper stearate	*1.16* / *4.75*	*1.19* / *4.64*	*1.23* / *4.21*	*1.25* / *4.19*	*1.19* / *4.10*	*1.09* / *4.05*	*0.93* / *3.90*

In the photo (see Fig. 3, item 1) it is shown that temperature decrease down to 160 °C during deformation of pro-oxidants containing cobalt stearate through the capillary with a length *l = 30 mm* promoted the extrudate surface distortion (see Fig. 3, item 1), i.e. a "sharkskin" surface defect characterized by the surface roughness, while the maximum pressure was recorded.

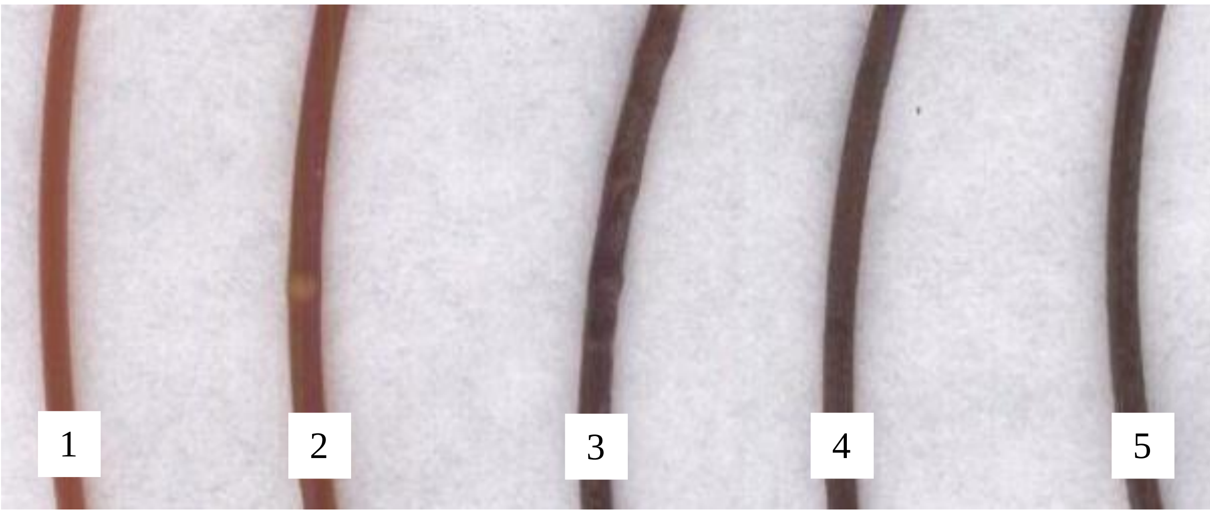
Analysis of the flow curves (Fig. 4), taking into account the presented tabular data (Table 1), allowed us to determine the processing temperature range, which is from 170 °C to 190 °C and is limited by flow instability, on the one hand, and destructive processes accompanied by gas release, on the other hand.

There are some stagnant zones in extrusion machines, in particular in the area of the head channels before the die mesh, which, in case of long residence times with compositions containing catalytic oxidation agents, contributes to production of products with strong adhesive properties. In this connection, studying technological properties and forecasting the behaviour of a material at critical processing parameters as a function of the thermal exposure time in extrusion equipment are of both theoretical and practical interest.

The influence of the thermal exposure time on pro-oxidant additives based on PVD 15803-020 polyethylene containing 10% by mass of variable-valence metal stearates was studied using a rheometer. The additive was fed into the rheometer chamber equipped with a piston, kept in it for 5 to 60 minutes, and then deformed through the capillary with a diameter d = 1 mm at a constant speed of 100 sec^{-1}. Figures 6 and 7 show photos of pro-oxidant additive extrudates containing iron stearate.

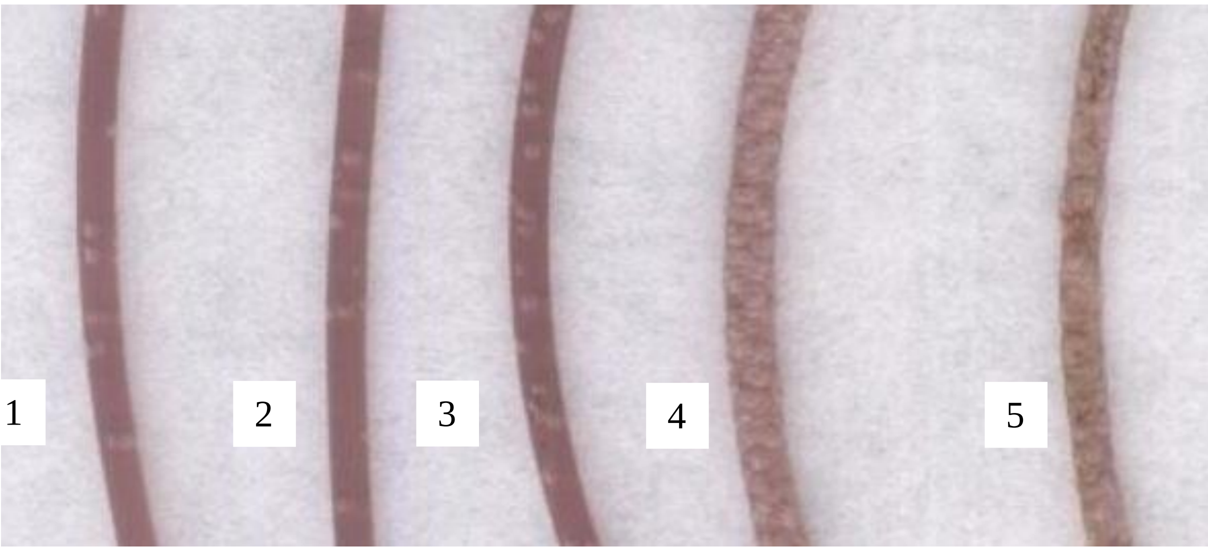
Longer thermal exposure in the rheometer chamber at a temperature of 190 °C promotes the formation of expanded extrudate structure, which is accompanied by darkening of extrudate surface for the additive containing iron (see Fig. 5) and a lighter surface for the additive containing cobalt stearate (see Fig. 6) due to entrapped gas bubbles.

High temperature and long thermal exposure intensify destruction processes, which are accompanied by gas release, on the one hand, and structurization, on the other hand, due to increase in the capillary pressure with exposure time, as indicated in Table 2.



1 – 5 minutes, 2 –10 minutes; 3 – 25 minutes; 4 – 40 minutes; 5 – 60 minutes

Figure 6: Photos of extrudates after deformation of pro-oxidant additive containing 10 % by mass of iron stearate through the capillary depending on the time of thermal exposure in the rheometer chamber.



1 – 5 minutes; 2 –10 minutes; 3 – 25 minutes; 4 – 40 minutes; 5 – 60 minutes

Figure 7: Photos of extrudates after deformation of pro-oxidant additive containing 10 % by mass of cobalt stearate through the capillary depending on the time of thermal exposure in the rheometer chamber.

Table 2: The effect of thermal exposure time on the change in the extrudate swell ratio /numerator/ and /denominator/ on pressurization during deformation of 15803-020 polyethylene and pro-oxidant additives on the basis thereof containing 10 % by mass of variable-valence metal stearates through the capillary (*d = 1 mm; l = 30 mm)*.

Name of material	Periods of pro-oxidant additive thermal exposure				
	5	10	20	40	60
15803-020 polyethylene	*1.22* *5.50*	*1.2* *5.30*	*1.2* *5.2*	*1.18* *4.5*	*1.13* *4.3*
Additive containing iron stearate	1.04 1.9	1.26 1.95	1.29 2.00	1.28 2.09	1.27 2.25
Additive containing cobalt stearate	1.08 3.20	1.15 3.2	1.18 3.2	1.55 3.2	1.62 3.2
Additive containing copper stearate	*1.11* *3.15*	*1.14* *3.30*	*1.18* *4.2*	*1.22* *4.5*	*1.12* *4.3*

Consequently, the processing time of pro-oxidant additive containing 10 % by mass of iron stearate should not exceed 10 minutes, as longer retention times lead to the extrudate expanded structure, dramatic change of its colour, and rough surface. Processing time for the additive containing copper or cobalt stearate is limited to 5 minutes due to strong extrudate surface defects being observed.

CONCLUSION

Thus, the limiting parameters of pro-oxidant additive production and processing are thermal exposure time, content of variable-valence metal stearates, and thermal exposure of the product during processing. For example, the thermal exposure time at a temperature of 190 °C is no more than 10 minutes for additives containing iron stearate and no more than 5 minutes for additives containing cobalt or copper stearate. A decrease in temperature below 170 °C for additives containing iron, copper or cobalt stearate allows longer thermo-mechanical exposure, but is limited by the unstable flow conditions showing up. When the content of pro-oxidants in the additives is 5% by mass and retention time no more than 15 minutes, during deformation in the rheometer, the flow curves in double logarithmic coordinates are invariant with respect to the geometric parameters of the capillary in the temperature range from 130 to 190 °C. Consequently, it is expedient to use high-speed extrusion equipment in the temperature range of 170 ÷ 190 ºC for production and processing of pro-oxidant additives containing no more than 10% by mass of variable-valence metal stearates.

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