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RESEARCH ARTICLE

OLIGOMERIC MECHANISM OF FILM BOILING ELIMINATION (EFB EFFECT) DURING METAL QUENCHING IN SOLUTIONS OF POLYISOBUTYLENE IN MINERAL OIL

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ABSTRACT

The results of a study of the cooling and rheological properties of solutions of oligomers and polymers polyisobutylene (PIB) in mineral oil are presented onwards. The concentration of PIB additives ranged from 0.25% by weight to 20.0% by weight while molecular mass (Mm) ranged from $4,0\cdot10^{2}$ m.u. to $6,0\cdot10^{4}$ m.u. It was established that in oligomeric PIB solutions with Mm from $0,68\cdot10^{3}$ to $1,0\cdot10^{4}$ there was a range of optimal concentrations in which there is a sharp reduction in the duration or complete elimination of film boiling (EFB effect) observed. In isoviscous solutions of PIB oligomers, an extreme dependence of the Inconel 600 thermal probe (TP) maximum cooling rate on Mm is observed, which is explained by the indirect influence of the geometric sizes of PIB macromolecules on the ratio of the density of the initial and critical heat fluxes caused by the first and second boiling crisis. A mechanism is proposed for the formation of an oligomeric heat-insulating film in the wall layer, which is responsible for the destruction of the vapor film (VF) and the transition to bubble boiling.

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INTRODUCTION

The first idea on possibility of regulating the duration of the film boiling process by obtaining a thin surface insulating layer on the metal surface was proposed by authors (Kobasko and Krivoshei, 1994, Kobasko. Moskalenko. 1996). In literature published by authors (Kobasko. Moskalenko, *et al.,* 1997, 2016, 2017; Lohvynenko. Moskalenko *et al.,* 2016) , this idea was experimentally confirmed when studying the effect of synthetic rubber (SKD) additives and PIB oligomers additives on the cooling capacity of I-12A and I-20A mineral oils. Theoretical aspects of a role of surface insulating layer on eliminating film boiling process was for the first time dissuaded by author (Kobasko. 2012). However, the question of the mechanism of thermo insulating layer (TIL) formation remains open (Lohvynenko. Moskalenko *et al.* 2017). The results obtained in (Lohvynenko Moskalenko *et al.* 2017). concerning the effect of the addition of low molecular mass PIB 680 and I-40A oil to the I-20A base oil showed that there is a minimum critical molecular mass (molecular mass PIB 680 and I-40A oil to the I-20A base oil showed that there is a minimum critical molecular mass (Mm_{cr}) below which oligomer additives do not remove completely the film boiling process. The aim of this work is to continue research on the mechanism of TIL formation and film boiling elimination during cooling of the cylindrical Inconel 600 TP in solutions of oligomers and low molecular mass PIB polymers in mineral oils.

Experimental results and discussion

Materials, instruments and experimental technique

- PIB oligomers with Mm = 400 (PIB 400), 680 (PIB 680), 1300 (PIB 1300), 2400 (PIB 2400), $1,0\cdot10^{4}$ (PIB 10^{4}) and also PIB polymers with Mm $2,0\cdot10^{4}$ (PIB $2,0\cdot10^{4}$) and $6,0\cdot10^{4}$ (PIB $6,0\cdot10^{4}$) were used as additives.
- Mineral oil I-20A.
- Facility and methodology (Lohvynenko. Moskalenko, *et.al,* 2016) .
- Rheology (Reotest 2, with digital indication of results)

Rheological properties of PIB solutions in mineral oil I-20A: Table 1 shows the results of studies of the dynamic

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viscosity of PIB solutions in I-20A oil in a wide concentration range at the temperature of 50°C and the shear rate of Dr = 729 sec^{-1}. According to the results of our calculations, there is a linear dependence of the shear stress (τr) on Dr over a wide range of temperatures and PIB content in oil, which allows PIB solutions to be attributed to Newtonian fluids (Gul', Kuznetsov, 1972). The Newtonian character of the flow indicates the absence of fluctuations in PIB concentration and density in the volume of solutions, which positively affects the uniformity of cooling products (Kobasko, 1980). Using the data from Table 1 for the convenience of analyzing the experimental results Fig. 1 shows the concentration dependences of the dynamic viscosity of PIB solutions in a graphical format.

The horizontal lines in Fig. 1 (1-5) determine $\eta_D{}^{50}$ values that are close to the dynamic viscosity values obtained experimentally for PIB solutions of the corresponding Mm, for which the cooling curves were obtained in parallel experiments, and the results are shown in Figs. 2-5 and in tables 2-5. The analysis of the concentration dependences of the rheological properties (Fig. 1, Table 1), temperature curves and thermal probe cooling rate, standard indicators of the cooling process (Fig. 2-5, Table 2-6) shows that there is a threshold concentration (C_{th},%) of additives upon reaching which a small increase of the solution viscosity is accompanied by a significant change in the main indicators of the cooling process: V_t^{max} and τ_{VF}. According to our calculations, the maximum decrease of τ_{VF} by 1.5 times upon reaching Ct was achieved for PIB 2400 solutions, while for low molecular mass PIB 680 solutions it decreased by 1.2 times. With an increase of concentration of PIB 2400 and PIB $1.0\cdot10^4$ additives above the Ct, the values of τ_{VF} approach τ_o, which determines the duration of the shock boiling stage and the initiation of the film boiling phase of the I-20A base oil. In this case, we can conclude that the film boiling is almost completely removed, i.e. the realization of EFB effect (Lohvynenko. Moskalenko, *et.al,* 2016,.2017); Kobasko. Moskalenko, *et.al.* 2016). A noticeable step remains on the cooling curves in PIB 680 solution after increasing concentration up to 10% by weight and more (Fig. 2, curves 5 and 6), which indicates the incomplete removal of VF while using oligomers with low molecular mass as additives. The introduction of the polymer additive PIB $2.0\cdot10^4$ into the I-20A base oil is accompanied by a significant increase of V_t^{max} values and a twofold decrease of τ_{VF} (Fig. 5, curves 6 and 8). However, with an increase of polymer concentration from 1.5% by weight up to 2.8% by weight, i.e. almost twice, the values of τ_{VF} change slightly. Thus, polymer additives with $Mm \geq 2.0\cdot10^4$ are not sufficiently effective with respect to the EFB effect, i.e complete VF removal.

Viscosity effect: It is known (Sheremeta*, et.al.,*1978; Tkachuk*, et.al.,* 1986, Rudakova*, et.al.,*1986) that the cooling properties of hardening substances are determined mainly by viscosity and wettability. Since PIB is not a surfactant (Lohvynenko. Moskalenko, *et.al,* 2016), attention should be paid to the role of rheological properties, which can affect the possibility of realizing the EFB effect. Fig. 6 shows the dependence curves of V_t^{max} versus Mm of PIB polymers and oligomers in a wide range of solution viscosity given by the concentration of additives As seen from Fig. 6, in isoviscous PIB solutions, an extreme dependence of V_t^{max} values on Mm additives is observed, while the range of $\eta_D{}^{50}$ values is from 19.0 to 22.8 mPa·s and Mm values range is from 1300 to $1,0\cdot10^4$ units inclusively, and it is optimal for all fractions.

Heat fluxes: Using the arrays of temperature curves of thermal probe cooling (Fig. 2-5), shown in Tables 2-5, the dependence of the density of heat fluxes on time (Fig. 7) and temperature (Fig. 8) was calculated by solving the inverse problem (IP) of thermal conductivity (Frenkel, 1975). As can be seen from the results shown in Fig. 7 and Fig. 8, the peak values of heat fluxes of isoviscous solutions of oligomers significantly increase with an increase in the molecular mass of PIB from 680 and 2400 m.u. to $1\cdot10^4$ and exceed by 1.5 times the *q* value obtained for the base oil I-20A. The *q* values obtained for the PIB $2,0\cdot10^4$ polymer solution reach the *q* values of PIB oligomeric solutions at a concentration of 2.8%, while the viscosity of the polymer solution is almost 2 times higher than the viscosity of oligomeric solutions (Fig. 1, Table 1). Considering that the viscosity of oligomer solutions is almost the same and is 30% higher than the viscosity of the base oil, this result can be explained by the indirect influence of the geometric sizes of PIB macromolecules on the ratio of the density of the initial and critical heat fluxes, which are caused by the first and second boiling crisis. According to the calculations, depending on the brand of oil and Mm of PIB, 3 to 7 macromolecules per 1000 molecules of mineral oil are enough to realize the EFB effect, which virtually eliminates the possibility of a significant effect on such parameters as heat capacity, heat and thermal diffusivity, latent heat vaporization and others (Frenkel, 1975).

EFB Mechanism: The authors (Kobasko, 2012; Lohvynenko. Moskalenko, *et.al,* 2016, 2017; Kobasko, Moskalenko, *et.al,* 2016) proposed a theory explaining the EFB effect by the formation of an oligomeric TIL on the metal surface, which decreases q_{IHF} (initial heat flux) below $q_{cr.1}$, resulting in a change in boiling modes (Kobasko, 1980). The above results allow us to clarify the mechanism of the EFB effect as follows: the formation of oligomeric TIL begins at the end of the stage of shock boiling. It is known (Tolubinsky, 1980) that at the moment of shock boiling a large number of small bubbles form and move from the surface of the metal into the volume of the coolant. The growth, advancement, and fusion of bubbles is accompanied by the formation of an adsorption layer of an oligomer or PIB polymer on their surface. An avalanche-like increase in the concentration of such bubbles ends with their merging and formation of a thin oligomeric or polymer film at the boundary between VF and PIB solution. At a certain concentration and Mm of the oligomer, TIL completely isolates VF from the solution; as a result, its recharge with oil vapor is significantly reduced. The pressure drop inside VF is naturally accompanied by its destruction, which creates the conditions for TIL to contact the metal surface under the influence of atmospheric pressure and causes the onset of heat transfer crisis and transition to bubble boiling (Kobasko, 2012; Lohvynenko, Moskalenko, *et.al,* 2017; Kobasko, Moskalenko, *et.al,* 2016; Gul' , 1972). It is known (Lipatov, 1972) that the structure and density of polymer's adsorption layers is determined by the concentration, stereochemistry, and Mm of macromolecules; therefore, the physicomechanical TIL indicators correspond to the selected composition of solution components. In this case, one should expect a significant effect of Mm of additives on the cooling process in PIB solutions, which is confirmed by the research results shown in Figs. 2-5 and in Tables 2-5. The proposed mechanism of the formation of TIL is confirmed by the inversion of the influence of the concentration of PIB additives on the solution cooling process's indicators. As seen in fig. 2-5, for all PIB solutions there is a concentration corresponding to the maximum cooling rate $C(V_t^{max})$, after which an increase in the content of the additive is accompanied by both a decrease in V_t^{max} and an increase in τ_{VF}. Apparently, an increase of the additive concentration above the optimum $C(V_t^{max})$ leads to the formation of a TIL with a loose structure, as a result of which its vapor permeability increases, and, consequently, the VF replenishment by oil vapor increases and leads to the inhibition of its destruction process. A change in the structure and density of TIL explains the existence of critical minimum ($Mm_{cr.}^{min}$) and maximum ($Mm_{cr.}^{max}$) molecular masses, which is confirmed by the results of studies of the cooling properties of solutions of low molecular mass PIB 400 and PIB $6{,}0\cdot10^4$ polymer in mineral oils (Fig. 9 and Fig. 10).

Analysis of the cooling curves and cooling rate shows that with an increase of the concentration of PIB 400 to 20% by weight a noticeable decrease of τ_{VF} and an increase of V_t^{max} are observed, however, the inhibition of the process of the film boiling phase removal is clearly seen. Therefore, the addition of low molecular mass PIB 400 to the oil shows itself as a viscous additive but not a structure-forming component. When PIB $6{,}0\cdot10^4$ polymer is added to the I-20A oil with increasing concentration (Fig. 10), insignificant changes of V_t^{max} and a noticeable effect on τ_{VF} are observed, both in the direction of increasing and decreasing of these indicators.

It can be assumed that the alternating effect of the concentration of PIB 6,0·104 polymer additives is due to the adsorption of macromolecules or fragments of their thermomechanical destruction on the metal surface, the presence of which can destabilize the heat transfer process (Liscic, Tensi *et al.,* 1992). However, in this case, it is difficult to explain the concentration dependences established above for the maximum cooling rate and the duration of the film boiling phase in oligomer solutions, especially the inversion phenomenon. Within the framework of the EFB mechanism proposed above, the complex behavior of Vt^{max} and τVF indicators in a polymer solution can be explained by the presence of local defects in the TIL structure, the probability of formation of which increases when the thermal probe is cooled in solutions of low molecular mass and high molecular mass PIB fractions (Lipatov, 1972).

RESULTS AND DISCUSSION

The question of the mechanism of the EFB effect, the integral part of which is the nature of TIL, is still debatable. In the early works (Sheremeta, *et.al.,* 1978; Tkachuk *et.al.,* 1986; Rudakova *et.al.,* 1986) special attention was paid to the problem of reducing the duration of the film boiling phase (FB), as a result of negative increase the quality of products after quenching. It was established (Sheremeta, *et.al.,* 1978) that the transition temperature from film to bubble boiling is determined by the average boiling temperature of the quenching medium, and high-molecular thermally unstable additives significantly reduce the duration of the vapor film phase. The effect is explained by an increase of pressure in VF during thermal destruction of such additives, which leads to a rupture of the solid oil film and transition to bubble boiling. However, such mechanism of vapor film destruction does not allow us to explain the experimental fact according to which the duration of FB phase and the boiling point of base oils change antibatically in the range of mineral oils I-8A, I-12A, and I-20A. The hypothesis of the formation of a thin TIL on the surface of a heated metal turned out to be fruitful and its real influence on the cooling process has been proved theoretically (Kobasko, 2012) and experimentally (Kobasko. Moskalenko, *et.al.,* 1997, 2016, 2017; Lohvynenko. Moskalenko, *et.al,* 2016).

However, the possibility of TIL formation and its effect on the heat transfer crisis in oligomeric solutions requires a detailed study (Lohvynenko. Moskalenko, *et.al,* 2017). If we assume that TIL arises and forms at the moment of shock boiling directly on the surface of a hot metal, then, according to (Khmelnitsky, *et.al.,* 1980), in the range of 700–800°C, the PIB film undergoes thermal destruction with the release of up to 70% of gaseous isobutylene monomer. Therefore, the effect of such a thin and short-lived TIL on the heat transfer crisis seems unlikely. The mechanism of TIL formation proposed by the authors limits the maximum temperature that affects the PIB film by the boiling point of mineral oil I-20A ($T_{boiling} = 350 \pm 20°C$), which corresponds to the initial stage of the thermal destruction process (Madorskiy. 1964). In this case, PIB additives practically do not come into contact with the hot metal; however, at the moment of shock boiling, they initiate the formation of TIL, the subsequent destruction of vapor film and the rapid onset of the heat transfer crisis.

The detailed analysis of the results given in the final Table 6 and in Fig. 6 shows that the maximum cooling rate Vt^{max} (°C/s) in isoviscous solutions of oligomers is observed at almost the same viscosity ($\eta_D{}^{50}{}_{=19{,}0\pm0{,}3\ \mathrm{mPa\cdot s}}$) for solutions of all PIB fractions. This can be explained by the existence of optimal hydrodynamic and thermodynamic parameters of oligomeric solutions, which make it possible to quickly transfer the stage of shock boiling to the phase of bubble boiling. With an increase in the molecular mass of PIB to Mm=2,0 10^4, which exceeds the Mcr. value, specific for each polymer (Mcr.PIB=1,7·10 4) (Barbenev1976) the hydrodynamic and thermodynamic parameters of polymer solutions significantly differ from oligomeric ones (Sanhalov, Minsker, 2001). This is manifested in a double increase of $\eta_D{}^{50}$ (Vtmax) and a 10–20% decrease of the cooling rate Vt^{max} (Table 6), while a noticeable shift corresponding to the film boiling phase remains on the cooling rate curve at high temperatures (Fig. 5).

The tendency toward a deterioration of the cooling properties of PIB solutions is clearly visible in the transition from oligomeric and "boundary" solutions (PIB $2{,}0\cdot10\ ^4$) to polymeric ones (Fig. 10). The addition of a relatively high molecular mass PIB $6{,}0\cdot10\ ^4$ to the oil slightly increases $V\ _t^{max}$ values and reduces τ_{VF} by 1.5–2.0 times, however, the film boiling phase does not completely remove. This can be explained by cardinal differences in hydrodynamic and thermodynamic parameters of polymeric and oligomeric solutions, because at values of Mm PIB above Mcr. limit a net of meshes is formed in solutions (Barbenev, 1976). The presence of such net, in addition to an abrupt increase of viscosity, can significantly affect the mobility and adsorption kinetics of PIB macromolecules at the boundary between vapor film and PIB solution (Lipatov. 1972) phases, and, consequently, the TIL formation process.

Table 1. Dynamic viscosity of PIB solutions in I-20A oil

	η^D (mPa·s) at concentration C (%) and temperature 50°C										
C. %	0.0	5.0	7.0	10.0	12.5	15.0	20.0				
PIB 400	14.26	14.89	15.21	15.58	16.12	16.31	16.99				
C. %	0.0	3.0	5.0	7.0	10.	12.5	19.0				
680	14.12	15.58	16.53	17.40	19.18	21.04	26.24				
C. %	0.0	3.0	5.0	7.5	10.0	12.5					
PIB 1300	14.48	16.94	18.63	21.50	24.64	28.15					
C. %	0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.5	5.0	7.5	10.0
PIB 2400	14.48	15.08	15.90	16.58	17.17	18.04	19.04	21.45	22.68	28.20	34.07
C. %	0.0	0.25	0.5	0.75	1.0	1.5	2.0	3.0	4.2		
PIB 10^4	14.49	15.21	15.90	16.94	18.17	19.81	22.27	27.33	34.56		
C. %	0.0	0.25	0.5	0.75	1.0	1.5	2.0	2.5	2.8		
PIB $2\cdot10^4$	14.39	15.58	16.99	18.40	20.13	23.50	27.60	31.43	34.56		
C. %	0.0	0.2	0.4	0.5	0.6	0.8	1.0				
PIB $6\cdot10^4$	13.57	16.53	19.68	22.55	23.50	27.97	33.89				

Table 2. Statistical indicators of the thermal probe cooling process (ISO9950) in solutions of PIB 680 polymer in I-20A oil at 50°C

№	Indicator (unit)	Cond.Design.	Concentration of PIB 680, % weight.						
			0	3.0	5.0	7.0	10.0	12.5	19.0
1	Probe Cooling Time from 850°C to 600°C, s	τ^{600}	8.1	6.7	5.7	5.4	5.2	5.2	5.4
2	Probe Cooling Time from 850°C to 400°C, s	τ^{400}	12.5	11	10.1	9.9	9.7	9.4	9.6
3	Probe Cooling Time from 850°C to 200°C, s	τ^{200}	35.4	34.5	34.2	34.6	34.7	33.9	35.7
4	Maximal cooling rate , °C/s	Vt^{max}	74.2	87.8	98.6	100.2	108.6	107.6	98
5	Temper. TP at max. cooling rate, °C	T_{TP}^{Vtmax}	576	602	632	667	645	647	632
6	Cooling rate at temper. TP=300°C, °C/s	$Vt^{T_{TP}300}$	9.4	8.8	8.7	8.7	8.5	8.5	8

Table 3. Statistical indicators of the thermal probe cooling process (ISO9950) in PIB 2400 oligomer solutions in I-20A oil at 50°C

№	Cond. Design.	Concentration of PIB 2400, % weight.					
		0	0.5	1	1.5	2	3
1	τ^{600}	8.1	7.8	5.7	5.3	4.7	3.5
2	τ^{400}	12.0	11.3	9.2	8.8	8.1	7.2
3	τ^{200}	37.3	36.3	34.7	35.7	34.5	34.7
4	Vt^{max}	74.7	88.4	103.4	111.8	108.8	119.4
5	T_{TP}^{Vtmax}	551	550	584	617	635	669
6	$V_t^{T_{TP}300}$	8.6	8.2	8.0	7.7	8.1	8.3

Table 4. Statistical indicators of the thermal probe cooling process (ISO9950) in PIB $1.0\cdot10^4$ oligomer solutions in I-20A oil at 50°C

№	Cond. Design.	Concentration of PIB $1\cdot10^4$, % weight.								
		0	0.25	0.5	0.75	1	1.5	2	3	4.2
1	τ^{600}	6.3	5.9	5	4.6	4.1	4.3	4.3	4.7	4.9
2	τ^{400}	9.7	9.1	8.1	7.9	7.2	7.5	7.6	8	8.6
3	τ^{200}	31.6	31.2	31.8	31.3	31.3	31.4	32.3	32.2	33.9
4	$V_t max$	78.5	98.5	108.2	104.8	117.4	119.5	116.5	114	96.7
5	T_{TP}^{Vtmax}	503	523	556	563	585	608	630	621	623
6	$V_t^{T_{TP}300}$	7.8	7.9	7.2	7.3	7.1	7.3	6.8	6.5	6.7

Table 5. Statistical indicators of the thermal probe cooling process (ISO9950) in PIB $2.0\cdot10^4$ oligomer solutions in I-20A oil at 50°C

№	Cond. Design.	Concentration of PIB $2\cdot10^4$, % weight.							
		0	0.25	0.5	0.75	1	1.5	2	2.8
1	τ^{600}	7.9	8.1	7.8	6.8	6.5	5.4	5.4	5.2
2	τ^{400}	11.9	12.3	11.8	10.9	10.3	9.4	9.7	9.8
3	τ^{200}	38.5	39.4	39.2	38.8	38.9	39.1	40.6	34.4
4	$V_t max$	79.5	79.7	83.5	88.3	87.5	97.3	97.6	100.2
5	T_{TP}^{Vtmax}	540	549	564	578	595	614	616	625
6	$V_t^{T_{TP}300}$	8.2	8.1	8.1	7.7	7.7	7.1	7	7.5

Table 6. Analytical indicators of the rheological properties and cooling ability of PIB solutions in I-20A oil

PIB in oil I-20A					
Indicator	PIB 680	PIB 1300	PIB 2400	PIB $1\cdot10^4$	PIB $2\cdot10^4$
C_{th}, %	3	1.5	1	0.25	0.75
$C_{Vt}{}^{max}$, %	10	5	3	1.5	2.8
$\acute{\eta}_D{}^{50}{}_{Vt}{}^{max}$, мPa·s	19.18	18.63	19.04	19.17	34.56
τ_{VF}, s	1	0.5	0.5	1.5	2
$V_t{}^{max}$, °C/s	108.6	129.8	119.4	120.6	100.2
$T_{TP}{}^{Vtmax}$, °C	645	649	669	608	625

C_{th} -threshold concentration of PIB, below which there is no effect of additives PIB in oil;
$C_{Vt}{}^{max}$ -concentration of PIB corresponding to the maximum cooling rate; $\acute{\eta}_D{}^{50}{}_{Vt}{}^{max}$ - the viscosity of the solution in which Vtmax is fixed;
τ_{VF} – the duration of vapor film (VF) phase; $V_t{}^{max}$ – the maximum cooling rate; $T_{TP}{}^{Vtmax}$ - thermal probe temperature at maximum cooling rate;

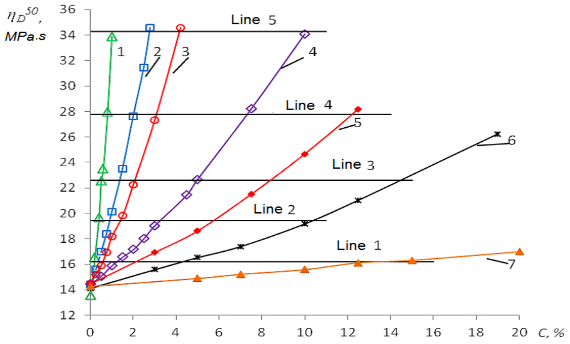

Fig. 1. The dependence of the dynamic viscosity η_D of PIB solutions in I-20A mineral oil on the concentration of additives at 50°C: 1-PIB 6,0·10^4; 2-PIB 2,0·10^4; 3-PIB 1,0·10^4; 4-PIB 2400; 5-PIB 1300; 6-PIB 680; 7-PIB 400

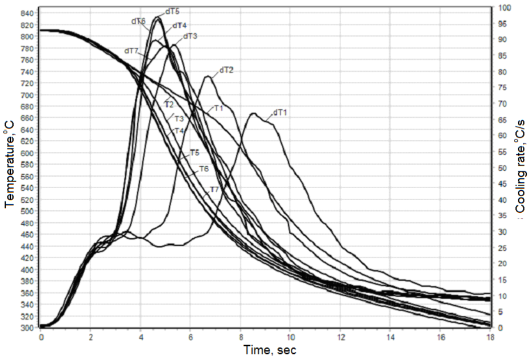

Fig. 2. Curves of temperature (T) and cooling rate (dT) of thermal probe in PIB 680 solutions in I-20A oil at 50°C, concentration,% weight: 1-0.0; 2-3.0; 3-5.0; 4-7.0; 5-10.0; 6-12.5; 7-19.0

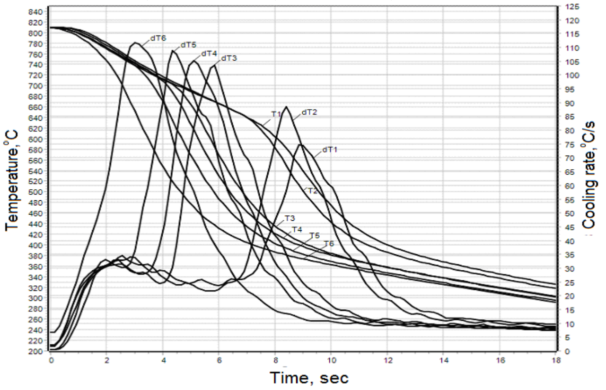

Fig. 3. Curves of temperature (T) and cooling rate (dT) of a thermal probe in PIB 2400 solutions in I-20A oil at 50°C, concentration, % weight: 1- 0.0; 2-0.5; 3-1.0; 4-1.5; 5-2.0; 6-3.0

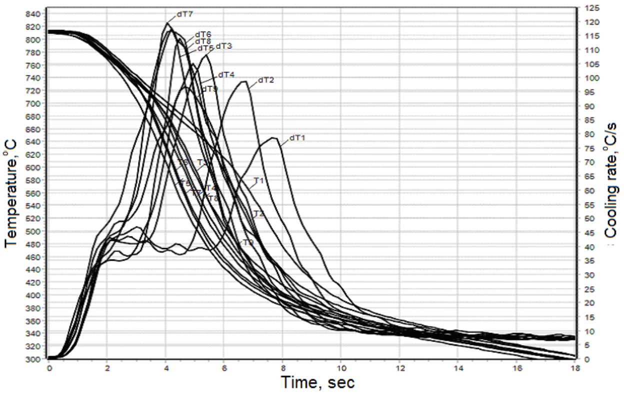

Fig. 4. Curves of temperature (T) and cooling rate (dT) of a thermal probe in PIB 1,0·10^4 solutions in I-20A oil at 50°C, concentration, % weight: 1-0.0; 2-0.25; 3-0.5; 4-0.75; 5-1.0; 6-1.5; 7-2.0; 8-3.0; 9-4.2

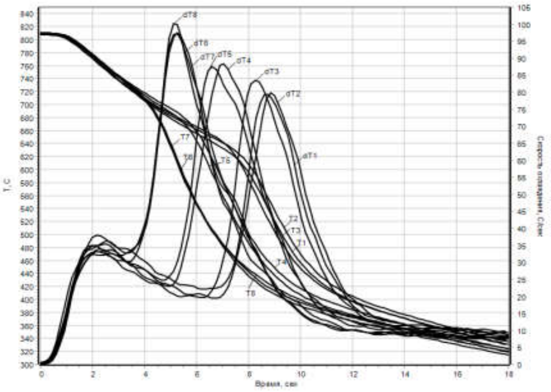

Fig. 5. Curves of temperature (T) and cooling rate (dT) of a thermal probe in PIB 2.0·10^4 polymer solutions in I-20A oil at 50°C, concentration, % weight: 1-0.0; 2-0.25; 3-0.5; 4-0.75; 5-1.0; 6-1.5; 7-2.0; 8-2.8

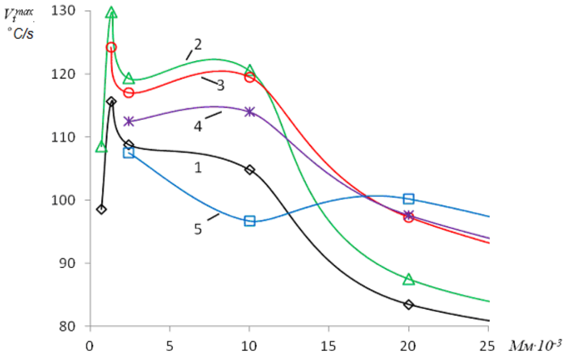

Fig. 6. Dependence of the maximum cooling rate of thermal probe $V_t{}^{max}$ on Mm PIB in isoviscous solutions of oligomers and PIB polymers in mineral oil I-20A0: 1 – $\eta_D{}^{50}$=16,20 mPa·s; 2 – $\eta_D{}^{50}$=19,44 mPa·s; 3 – $\eta_D{}^{50}$=22,60 mPa·s; 4 – $\eta_D{}^{50}$ = 27,77 mPa·s; 5 - $\eta_D{}^{50}$ = 34,27 mPa·s

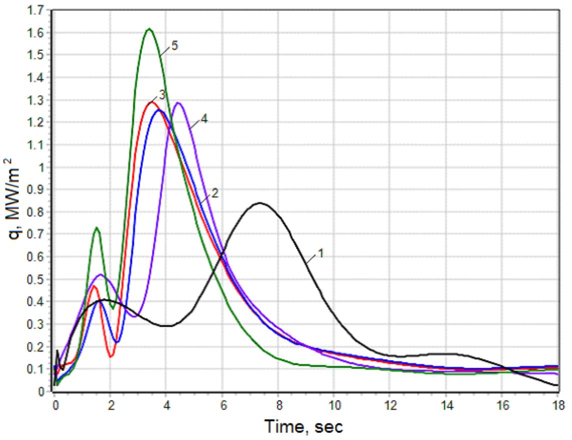

Fig.7. Kinetics of heat flux density for various quenchants: 1 - I-20A; 2 – 10% PIB 680; 3 – 3% PIB 2400; 4 – 1,5% PIB $1\cdot10^4$; 5 – 2,8% PIB polymer $2\cdot10^4$

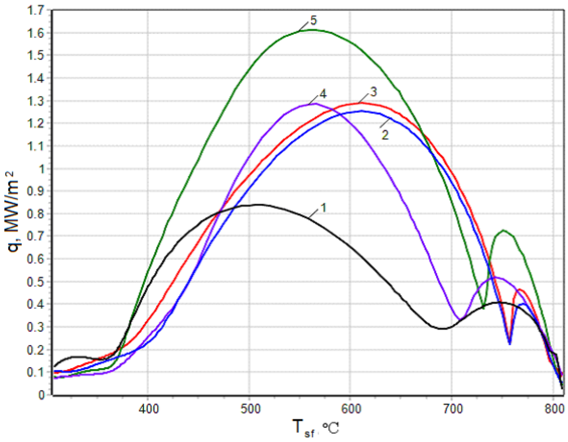

Fig.8. Variation of heat flux density for various quenchants: 1 - I-20A; 2 – 10% PIB 680;3 – 3% PIB 2400; 4 – 1,5% PIB $1\cdot10^4$; 5 – 2,8% PIB polymer $2\cdot10^4$

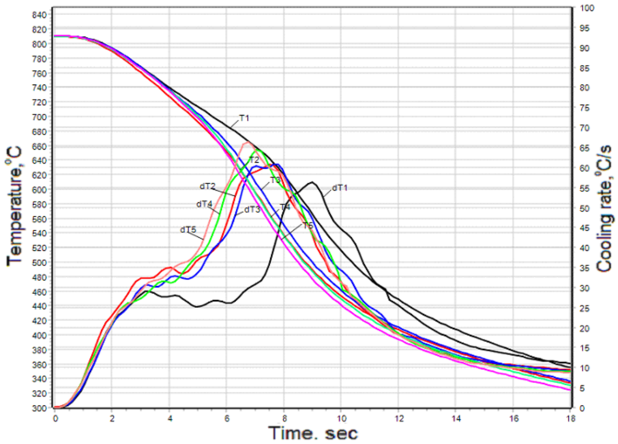

Fig. 9. Curves of temperature (T) and cooling rate (dT) of a thermal probe in PIB 400 solutions in I-20A oil at 50°C, concentration, % weight: 1-0.0; 2-5.0; 3-10.0; 4-15.0; 5-20.0

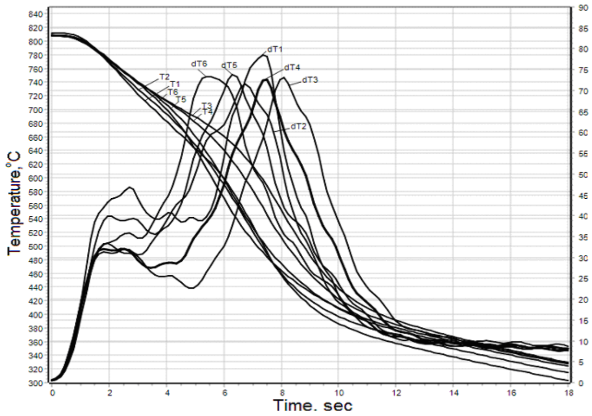

Fig. 10. Curves of temperature (T) and cooling rate (dT) of thermal probe in PIB $6,0\cdot10^4$ solutions in oil I-20A at 50°C, concentration, % weight: 1-0.0; 2-0.2; 3-0.4; 4-0.6; 5-0.8; 6-1.0

Conclusion

- There is a threshold concentration (C_T) of PIB oligomers, upon reaching which a slight increase of the solutions viscosity is accompanied by a significant shift of the cooling process indicators $V_t^{\ max}$ and τ_{VF}. With an increase of PIB's Mm from 680 m.u. to $1.0\cdot10^4$, the values of C_T reduce by 12 times, which is explained by the specific of the process of forming an oligomeric thermo-insulating film (TIL) at the boundary between vapor film and PIB solution phases.
- At the moment of shock boiling at a certain concentration and Mm of the oligomer the TIL is practically isolates VF from the solution, reduces its recharge with oil vapor which leads to VF destruction. This creates conditions for TIL to contact the metal surface under atmospheric pressure. The appearance of a thermal barrier on the metal surface creates thermal resistance, which causes the onset of the heat transfer crisis and the transition to bubble boiling.
- The peaks on the concentration dependences $Vt^{\ max}$ (°C/s) are observed at the same viscosity of oligomeric solutions; therefore, in this interval, the hydrodynamic stability of the phases border surface is violated, which is a necessary condition for the film boiling crisis (Berlin,. Kalinin *et al.,* 1973).
- The extreme dependence of the maximum cooling rate and the duration of the film boiling phase on Mm oligomers is explained by the optimal geometric sizes of the PIB 1300, PIB 2400, and PIB $1.0\cdot10^4$ macromolecules, as a result of which a TIL of the corresponding structure and density is formed.
- The minimum $Mm_{cr}^{\ .min}$ = 680 m.u. and the maximum $Mm_{cr}^{\ .max} = 1.0\cdot10^4$ m.u. critical molecular mass of PIB is determined, below and above which the effect of EFB is not realized. According to (Sanhalov Minsker, 2001; Berlin, 2002), oligomers are substances that contain a large number of repeating units, and their total Mm should be in the range of $5\cdot10^2$ - $5\cdot10^4$ m.u. The interval between $Mm_{cr}^{\ .min}$ and $Mm_{cr}^{\ .max}$ of PIB falls into this range; therefore, the EFB effect is realized due to the existence of oligomers, i.e. oligomeric state of the substance (Berlin. 2002). It is known (Mezhikovsky, 2005) that aggregates appear in oligomeric solutions, which are characterized by a high orientational order of oligomeric molecules. Apparently, this characteristic of oligomeric solutions explains their unique ability to radically affect the metal quenching process.

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