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Effect of self-heating during processing of rigid and plasticized poly(vinyl chloride) on its thermal stability

RAPID COMMUNICATION

Summary — Times of dynamic thermal stability (τ_t) depending on real temperatures of poly(vinyl chloride) (PVC) melts with different viscosities were investigated and compared. The experimental data were analyzed using the Arrhenius equation and the activation energy of PVC dehydrochlorination was determined. It was found that increased thermal stability of the melts caused by plasticization is related to a decrease in their self-heating.

Keywords: poly(vinyl chloride), thermal stability, composition, plasticization.

WPLYW SAMONAGRZEWANIA PODCZAS PRZETWARZANIA SZTYWNEGO I UPLASTYCZNIONEGO POLI(CHLORKU WINYLU) NA JEGO STABILNOŚĆ TERMICZNĄ

Streszczenie — Zbadano i porównano czasy dynamicznej stabilności termicznej (τ_t) w zależności od rzeczywistej temperatury stopów (T_p) poli(chlorku winylu) (PVC) i jego kompozycji różniących się lepkością. Uzyskane wyniki opisano za pomocą równania Arrheniusa, wyznaczając energię aktywacji procesu odchlorowodorowania. Stwierdzono, że stabilność termiczna stopów uplastycznionego PVC jest związana ze zmniejszonym efektem ich samonagrzewania.

Słowa kluczowe: poli(chlorek winylu), stabilność termiczna, kompozycje, uplastycznianie.

Highly viscous polymeric materials can be self-heated during mixing and processing (as a result of energy dissipation at intensive deformation). It additionally increases temperature and accelerates thermal degradation of the molten polymer. So self-heating complicates the manufacture of products made from such polymeric materials. Rigid poly(vinyl chloride) (PVC) is a material of that type. It is processed by injection molding and extrusion and is widely used in manufacturing of pipes, sidings, panels, pipeline fittings of different sizes, *etc.*

Thermal stability of PVC materials is one of the most important technological characteristics, which requires optimization of the processing parameters and the PVC recipes.

Usually thermal stability of PVC is tested using the „Congo red” method according to ISO 182/1 standard (static thermal stability) or using the Brabender plastograph (dynamic thermal stability) [1, 2]. The prolonged

time of dynamic thermal stability [2, 3] provides conditions for safe processing. It depends on deformation conditions of the PVC melt and is significantly reduced with increasing melt temperature. Additional self-heating of PVC melt leads to a decrease in the time of thermal stability and worsens the processing conditions of rigid PVC [4, 5]. The viscosity of molten rigid PVC, containing thermal stabilizers only, reaches $4 \cdot 10^3$ Pa·s at processing temperatures. Often it cannot be processed by injection molding and extrusion due to the high temperature and thermal degradation [3]. To regulate the rheological properties of PVC melts and to decrease its viscosity, a balanced system of lubricants and plasticizers with different thermodynamic compatibilities must be introduced into such compositions. Usually depending on the thermodynamic compatibility the additives to PVC can be divided into the following groups: plasticizers with unlimited compatibility and lubricants with limited compatibility [6, 7]. Many investigations of the effect of plasticization on decrease in viscosity of PVC melts are described [8, 9].

The purpose of this work was investigation and comparison of the times of dynamic thermal stability measured depending on real temperatures of PVC and its composition melts of different viscosities, rather than depending on the temperature in the plastograph chamber.

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EXPERIMENTAL

Materials

Stabilized compositions based on slurry PVC resin S-58 with K value 58 ($\overline{M}_n = 44\,000$, $\overline{M}_w/\overline{M}_n = 2.27$), produced by Kaustik (Sterlitamak, Russia) were chosen as the object of this research. The main rigid PVC composition contained 3 phr of Ca/Zn thermal stabilizer composed of 1 phr calcium stearate and 2 phr zinc stearate, both were supplied by SZHR (Stavropol, Russia). Plasticizer dioctyl phthalate (DOP) – a transparent oily liquid (with density $d = 0.985\text{ g/cm}^3$ at $20\text{ }^\circ\text{C}$) was delivered by Salavatneftesintez (Salavat, Russia). Plasticizer was added to plasticized PVC compositions in the amount between 5.5 and 44.5 phr.

Methods of testing

To prepare the PVC blends rotating torque rheometer-mixer Plastograph[®]-FDO234S produced by Brabender GmbH (Duisburg, Germany) with a torque measuring range of $200\text{ Nm} \pm 0.1\%$ and the chamber volume of 30 cm^3 was used. The plastograph was supplied with a detector to measure the amount of hydrogen chloride (HCl) released during thermal degradation with the conductometric method described in [2]. Experiments were carried out at the temperatures of the plastograph chamber (T) between 180 and $210\text{ }^\circ\text{C}$, the rotation speeds of rotors (n) was between 10 and 90 rpm and constant charge was 20 g . We accepted the time of the induction period defined by the time of appearance of HCl (determined with the error of $\pm 0.5\text{ min}$) as the time of dynamic thermal stability (τ_t) of PVC compositions. The time τ_t should be longer than the processing time of PVC material in an extruder or molding machine. The real temperature of melt (T_f) during mixing was measured by the pyrometer CEM DT-8812 (China) with the temperature measuring range from -50 to $500\text{ }^\circ\text{C} \pm 2.0\%$ and measuring time $\leq 1\text{ s}$. The noncontact measurements of the melting temperature at established torque were performed with the open plastograph chamber without discontinuation of mixing (the chamber was opened for a short time and closed again). Additional increase in the melt temperature (ΔT) was calculated as the difference: $\Delta T = T_f - T$.

Rheological studies were carried out with the use of a capillary viscometer UMI-2 Götffert (Buchen, Germany) and used to determine the melt mass-flow rate (MFR) of a thermoplastic material according to ASTM D 1238 standard. It is based on the measurement of the mass of the material that was extruded from the die (length 8 mm , diameter 2.095 mm) over the given period of time, piston load 21.6 kg and $180\text{ }^\circ\text{C}$ and it is expressed in $\text{g}/10\text{ min}$.

RESULTS AND DISCUSSION

The dependence of the dynamic thermal stability time (τ_t) of rigid PVC on the rotation speed for different tem-

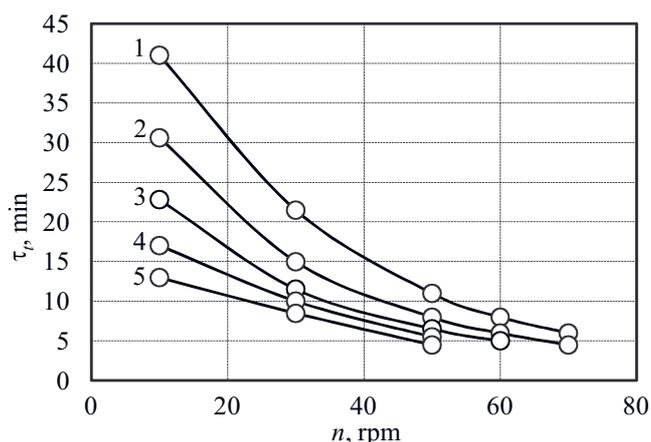


Fig. 1. The dependence of the dynamic thermal stability time (τ_t) of rigid PVC melt on the rotation speed (n) for different temperatures of the chamber (T): 1 – $180\text{ }^\circ\text{C}$, 2 – $185\text{ }^\circ\text{C}$, 3 – $190\text{ }^\circ\text{C}$, 4 – $200\text{ }^\circ\text{C}$, 5 – $210\text{ }^\circ\text{C}$

peratures of the plastograph chamber is shown in Fig. 1. Values of τ_t are reduced significantly with increasing rotation speed and the temperature of plastograph mixing chamber (T). However, at the rotation speed greater than 30 rpm , τ_t depends a little on T in the range between 180 and $210\text{ }^\circ\text{C}$. This effect points at the influence of additional self-heating of PVC melts.

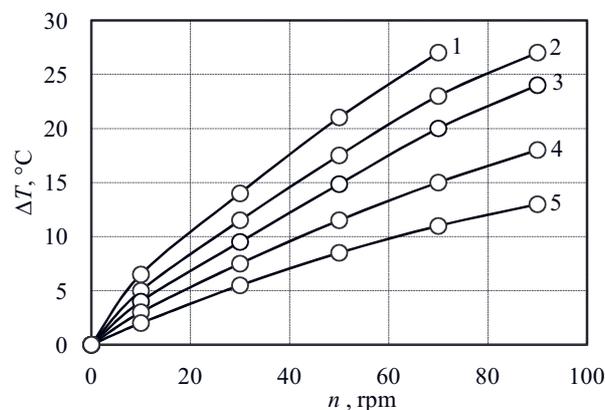


Fig. 2. Dependence of additional temperature increase (ΔT) of rigid PVC melt on rotation speed (n) at different temperatures of the chamber: 1 – $180\text{ }^\circ\text{C}$, 2 – $185\text{ }^\circ\text{C}$, 3 – $190\text{ }^\circ\text{C}$, 4 – $200\text{ }^\circ\text{C}$, 5 – $210\text{ }^\circ\text{C}$

Figure 2 shows the temperature increase as a result of self-heating (ΔT) of rigid PVC melts at different processing parameters. ΔT of the PVC melt increases when the temperature of plastograph chamber (T) goes down and the rotation speed (n) goes up. The results can be explained by the following relationship between the amount of heat emitted by the melt (g) and the values of melt viscosity (η) and shear speed ($\dot{\gamma}$) [10]:

$$g = f(n\dot{\gamma}^2) \quad (1)$$

Increase in the melt temperature at intensive stirring can reach 20 deg and more. This effect may have a great influence on the dynamic thermal stability and may lead to break of the technological process and spoilage. Decrease in the PVC melt viscosity at high temperatures can lead to decrease of ΔT , that is why at 210 °C ΔT is only 2–13 deg (technological hazard). Safe processing conditions of tested rigid PVC are provided when the rotation speed is not higher than 30 rpm and the self-heating is minimum.

Table 1. Effect of the plastograph chamber temperature (T) in additional temperature increase (ΔT) and time of dynamic thermal stability (τ_t) of rigid PVC melt without addition of DOP ($n = 50$ rpm)

$T, ^\circ\text{C}$	180	185	190	200	210
$\Delta T = T_f - T, \text{ deg}$	22	18	15	12	8
$T_f, ^\circ\text{C}$	202	203	205	212	218
$\tau_t, \text{ min}$	12	9	8	6	5

Table 1 shows the values of ΔT and τ_t of rigid PVC melts for different initial temperatures of the chamber (T) and the real melt temperatures (T_f). ΔT values decrease with increase in T because the self-heating effect becomes weaker.

Table 2. Effect of DOP content on $MFR, \Delta T$ and τ_t of plasticized PVC melt ($T = 180$ °C, $n = 50$ rpm)

Content of DOP phr	0	5.5	11.5	18.5	26	44.5
$MFR (180$ °C, 21.6 kg), g/10 min	4.5	9.3	27.4	76.7	370	>1000
$\Delta T = T_f - T, \text{ deg}$	22	15	11	7	3	<1
$T_f, ^\circ\text{C}$	202	195	191	187	183	~180
$\tau_t, \text{ min}$	12	20	27	32	42	49

Table 2 shows the data illustrating the influence of DOP content on MFR and τ_t of plasticized PVC melts during mixing at the constant chamber temperature. The plasticization decreases viscosity determined by MFR and ΔT , therefore τ_t is increased.

PVC is the object of thermodestruction in all PVC compositions, therefore Fig. 3 shows that all experimental points plotted on the graph $\ln \tau_t = f(1/T_f)$ lie on a straight line. This indicates that the main factor affecting the thermodegradation of PVC in the plasticized and rigid compositions is the real temperature of melt which is related to the chamber temperature or plasticizer content. We can draw the conclusion about the mechanism of the processes analyzing the observed dependence with the Arrhenius equation:

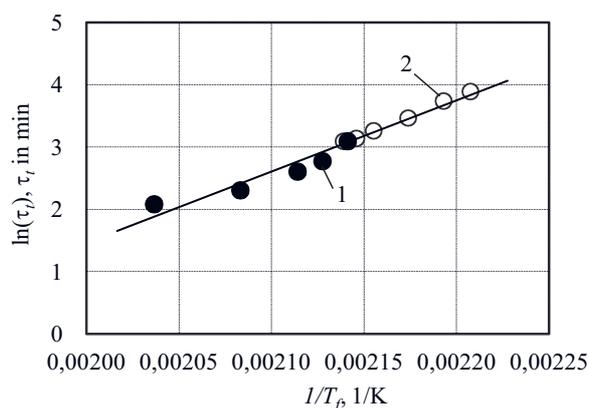


Fig. 3. The dependence of the dynamic thermal stability (τ_t) on real temperature of PVC (T_f): 1 – rigid PVC (Table 1), 2 – plasticized PVC composition (Table 2)

$$\ln \tau_t = E / RT_f \quad (2)$$

where: E – thermal coefficient, R – universal gas constant.

It is known that activation energy (E_a) of PVC dehydrochlorination process takes up to 118–139 kJ/mol [10, 11]. The E coefficient obtained from the data given in Fig. 3 is 128 ± 2 kJ/mol. As it is expected, it is close to the E_a value of PVC dehydrochlorination. Nonlinearity of the experimental dependence observed for small τ_t on Fig. 3 may be associated with the increase in warming up time of the material in the chamber to a stable temperature (2–3 min).

CONCLUSIONS

The dynamic thermal stability of PVC materials depends not only on the recipe of PVC composition but also on the effect of the self-heating during processing. Increase of dynamic thermal stability under plasticization is associated with reduction in melt viscosity and decrease in melt self-heating. Thus the introduction of a plasticizer leads to the increase of the dynamic thermal stability as it decreases melt self-heating.

The self-heating effect should be taken into account when one chooses a PVC type and optimizes the system of stabilizers, plasticizers, lubricants and also technological parameters of PVC processing.

The work was supported by the Ministry of Education and Science of the Russian Federation – Federal program „Investigations and elaborations for priority trends in development of the scientifically-technological complex of Russia during 2007–2013 years“.

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Received 29 V 2012,
in revised form 9 IV 2013.

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