

## MATERIALS SCIENCE. CORROSION PROTECTION

### EFFECT OF SUPERCOOLING AND SHEAR STRESS ON THE PROPERTIES OF POLYAMIDE-12

**Yu. A. Taran and A. A. Solovyev**

UDC 66.065.5

The influence of the dynamics of the polymer materials crystallization process on its properties was investigated. The crystallization process was studied in two cases: during supercooling, and during supercooling together with applied shear stress. The impact of shear stress and supercooling on the crystallization kinetics was studied. The experiment was carried out using two techniques: differential scanning calorimetry and rheometry. Polyamide-12 was chosen as the object of research. The data were processed by the method developed by the authors. The following parameters were determined: induction period, rates of nucleation and growth.

**Keywords:** polymers; crystallization kinetics; polyamide-12, formal analogy, DSC, rheometry.

Kinetics of crystallization of thermoplastics has been studied since the late 50s – early 60s of the 20th century. However, the study of crystallization of polyamide-12 (PA-12) began only in the early 2000s. So, in [1], a cross experiment on the study of crystallization kinetics was conducted by differential scanning calorimetry (DSC) and high-temperature microscopy in isothermal and non-isothermal modes. With the development of the additive technology of selective laser sintering (SLS), this issue has been getting more attention both relating to investigations of the SLS process [2–4] and the study of crystallization kinetics as a whole [5, 6].

It is important to note that in traditional methods of plastics processing, such as extrusion or injection molding, not only supercooling, but also shear stress applied during the process greatly influence the properties of the final product.

Despite the influence of shear forces on all kinetic parameters of the crystallization process: induction period, nucleation and crystal growth rates [7–9], there are very few publications [10, 11] that describe the combined effect of supercooling and shear stress on the crystallization process of polymeric materials. The relevance of this topic is also due to the fact that over the past 10 years several articles have been published on the rheodsc method (combining rheology with differential scanning calorimetry) [12, 13], however, the equipment used to implement this method has not been widely used, probably due to high cost and technical complexity of manufacturing.

At the same time, the question of calculating the kinetic parameters of the crystallization process remains open: the induction period, rates of nucleation and growth of crystalline formations. The methodology for calculating these parameters is given in [14], however, this is not enough for a comprehensive review of this issue as it applies to the object of our investigation.

---

Russian Technological University (MIREA), M. V. Lomonosov Moscow State Academy of Fine Chemical Technology, Moscow, Russia; e-mail: mongousse2@yandex.ru.

---

Translated from *Khimicheskoe i Neftegazovoe Mashinostroenie*, Vol. 56, No. 1, pp. 35–38, January 2020.

The purpose of this work is to develop a methodology for studying the crystallization kinetics of polymeric materials, taking into account the effects of both supercooling and shear stress without using the difficult to access rheodsc technology, as well as application of the obtained generalized technique to determine the crystallization kinetics of polyamide-12 and compare the results with the existing data from other authors.

### **Method for Determining Crystallization Kinetics Parameters**

To determine the crystallization kinetics parameters of plastics under the influence of supercooling and shear stress, a joint technique is used that combines the method of differential scanning calorimetry (DSC) with the rheometry method.

The DSC method allows one to obtain a curve of the degree of completion of the thermal effect (degree of crystallinity) versus the duration of the crystallization process according to the standard method. The studies were performed on a Perkin Elmer DSC 8500 differential scanning calorimeter. However, when using this method, it is impossible to subject the sample to shear stress.

This drawback can be compensated by studying the effects of shear stress on a RheoStress series rheometer from Thermo Haake. To implement this technique, a rheometer with an oscillation mode and a set of cone~—plane geometries is required.

The mass of the sample in the DSC method is less than in the rheometry method, so one should use the smallest available measurement geometry in the rheometry method and take into account the characteristics of this geometry.

Oscillation mode is a mode in which the sample is deformed at a frequency of 1 Hz by 1 degree. This is the gentlest shear regime that makes it possible to minimally deform the resulting crystalline structure. This mode, when conducting an experiment at a temperature close to the crystal – melt phase transition, can be compared with studies performed by the DSC method, since the structure is almost not deformed, which allows one to compare the data of DSC and rheometry methods.

*The essence of the method proposed by the authors is as follows:* the polymer under study is crystallized and kinetics is studied by the DSC method at various temperatures. The smaller the temperature increment, the more complete data can be obtained. The sample is also studied by rheometry at temperatures set in the DSC method, but at different shear rates. Evidently, the smaller the shear rate increment, the more data can be obtained. The increments in temperature and shear rate are selected individually for each polymer.

As a result of this series of experiments, a series of curves are obtained showing the dependence of the degree of completion of the thermal effect on the duration of the crystallization process (in the DSC method) and the complex module on the duration of the crystallization process (in the rheometry method).

Based on these data, using the methodology of [9, 15, 16], it is possible to calculate the desired parameters — the induction period of the crystallization process, the nucleation and crystal growth rates.

An important advantage of this method is that it uses granules that have not yet been processed, that is, granules without a thermal history that have never crystallized.

### **Materials and Methods of Research**

Rilsan brand polyamide-12 manufactured by Arkema was used as the test material.

Samples for DSC were sections of granules weighing 2–3 mg (0.002–0.003 g). The studies were carried out in the isothermal crystallization mode [17]: the sample was heated to a temperature of 200°C (which is 20°C higher than the melting point of PA-12 (178°C)) and held at this temperature for 10 min in order to obtain

a homogeneous melt without crystalline structures. Then the sample was cooled to temperatures of 165, 160, 155°C, respectively. During cooling, the difference in heat flux between the PA-12 sample and the standard sample was measured.

For rheometry studies, granules with a total mass of 0.3 g were used. Such a difference in the mass of samples is due to the need to fill the working gap of the rheometer for research. As the measuring geometry, the cone — plane system with a diameter of 35 mm with a taper angle of 1° was chosen.

The experiment was carried out as follows: the test sample was placed in the gap of the measuring geometry and heated to a temperature of 200°C, similarly to the DSC method. Then, the sample was cooled to temperatures of 165, 160, 155°C, after which the change in the elastic component of the complex elastic modulus was measured by analogy with the study [11]. The measurements were carried out in the oscillation mode and with shear rates of 1, 2, 5 sec<sup>-1</sup> at temperatures of 165, 160, 155°C.

### Data Analysis Method

When applying the developed methodology and the Kolmogorov–Avrami equation, preliminary processing of the obtained experimental time dependences of the heat flux  $H = f(\tau)$  is necessary.

The obtained experimental data must be processed according to the equation

$$X_t = \frac{\int_0^t \left( \frac{dH}{dt} dt \right)}{\int_0^\infty \left( \frac{dH}{dt} dt \right)}, \quad (1)$$

where  $H$  is the heat flux, mW.

There is no need for such processing of data obtained by the rheometry method, since a sigmoid curve is already obtained during the experiment. Physical and computational experiments are based on the probabilistic nature of the process.

The first calculation step is to determine the induction period of the crystallization process  $\tau_{\text{ind}}$  (the period when the crystallization process has already begun). It is not possible to trace the induction period, and there are no changes on the dependence  $\eta = f(\tau)$  (the graph remains parallel to the x axis).

The second calculation step is the calculation of the nucleation rate of crystalline structures  $\varpi_n = f(T)$  according to formula (2) and the dependences of the nucleation rate on supercooling and shear stress  $\varpi_n = f(\Delta T)$  and  $\varpi_n = f(\Delta G')$

$$\varpi_n = \frac{1}{\tau_{\text{ind}} V}, \quad (2)$$

where  $\tau_{\text{ind}}$  is the induction period of the process, sec;  $V$  is sample volume, m<sup>2</sup>.

Next, the linear growth rate of the crystal structures  $v_\Lambda$  is determined using the Kolmogorov–Avrami equation for both cases

$$\eta(\tau_k) = 1 - \exp(-K\tau_k^{n+1}), \quad (3)$$

where  $\eta(\tau_k)$  is the degree of crystallinity, %;  $K$  is the crystallization rate constant of crystalline structures;  $n$  is the crystal growth coefficient;  $\tau_k$  is the duration of the crystallization process, sec.

Considering the growth of crystalline structures as layered ( $n = 3$ ), and the resulting crystalline structures as spherical, we transform equation (3) into

$$v_{\Lambda} = \left[ \left[ -\ln [1 - \eta(\tau_k)] \frac{n+1}{\beta \varpi_n \tau_k^{n+1}} \right]^{1/n} \right], \quad (4)$$

where  $v_{\Lambda}$  is the linear growth rate of crystalline structures, m/sec;  $\beta$  is the coefficient characterizing crystal shape.

When determining all the necessary parameters from equations (2), (4), we evaluate the effect of the change in the shear rate applied to the sample upon supercooling on the change in the rates of nucleation ( $\varpi_n$ ) and growth ( $v_{\Lambda}$ ) of crystal structures.

The ascending branches of the dependences  $\varpi_n$  and  $v_{\Lambda}$  (as in the case of other transformations with structural rearrangement of the initial system) are well described by power-law dependencies [16] and can be obtained by the following equations:

$$\varpi_n = B_n (\Delta T)^n, \quad (5)$$

$$v_{\Lambda} = B_{\Lambda} (\Delta T)^n, \quad (6)$$

$$\varpi_n = B_n (\Delta G')^n, \quad (7)$$

$$v_{\Lambda} = B_{\Lambda} (\Delta G')^n. \quad (8)$$

## Research Results and Discussion

Consider the effect of shear rate on the crystallization process of polyamide-12. The dependences of the degree of crystallinity on the duration of the crystallization process are presented in Fig. 1.

From the graphs in Fig. 1 it can be seen that with increasing shear rate, the duration of the crystallization process decreases. An increase in supercooling also accelerates the crystallization process. Since the duration of the process decreases significantly (by about a factor of 2) (when comparing the data obtained in the oscillation mode and the data obtained in the mode with a shear rate of  $5 \text{ sec}^{-1}$ ), the induction period of the crystallization process also decreases.

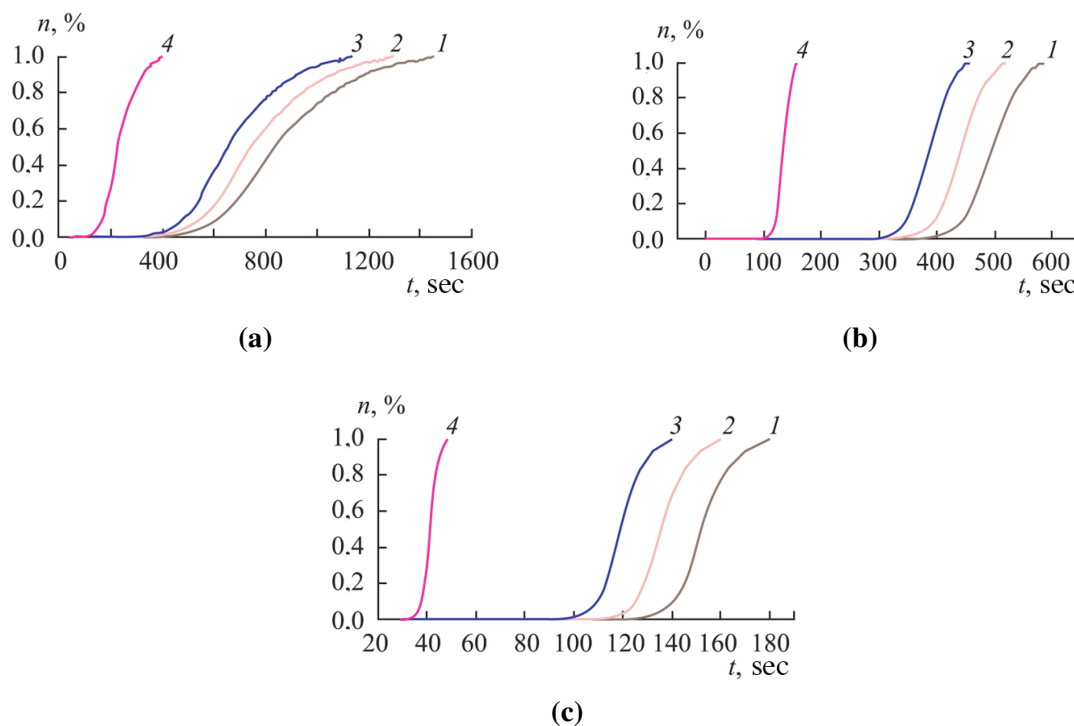
Figure 2 shows the dependences of the rate of nucleation of crystalline structures on the shear rate at temperatures of 165, 160, 155°C.

The rate of nucleation of crystalline structures increases substantially with an increase in supercooling, as well as with an increase in the shear rate.

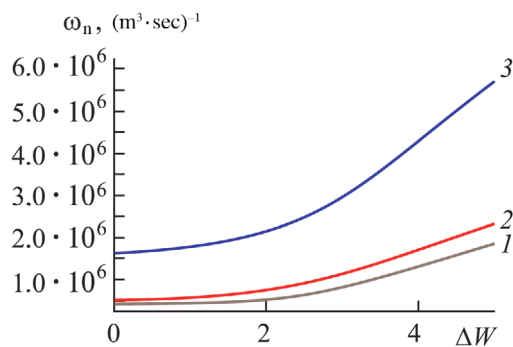
Figure 3 shows the dependences of the growth rate of crystalline structures on shear rate at temperatures of 165, 160, 155°C.

The growth rate of crystalline structures increases significantly with increasing supercooling, as well as with an increase in shear rate. An insignificant change in the growth rate of crystalline structures is noted at shear rates of  $1 \text{ sec}^{-1}$  and  $2 \text{ sec}^{-1}$ .

The research results can be useful in improving technological processes for processing polyamide-12 by extrusion and injection molding (to improve product properties), as well as in the development and implementation



**Fig. 1.** Dependences of the degree of crystallinity of PA-12 on the duration of the crystallization process at a temperature of 165°C (a), 160°C (b), 155°C (c); DSC mode – 1; oscillation mode: 2 – 1 sec<sup>-1</sup>; 3 – 2 sec<sup>-1</sup>, 4 – 5 sec<sup>-1</sup>.

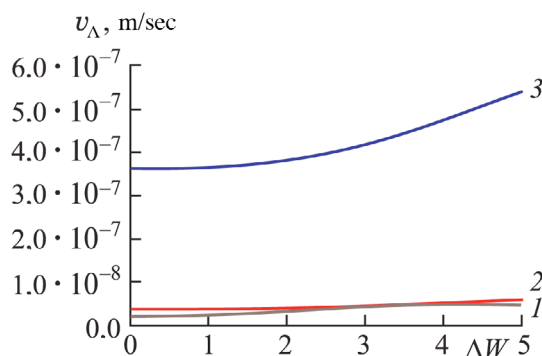


**Fig. 2.** Dependences of the rate of nucleation of crystalline structures  $\omega_n$  of PA-12 on shear rate at temperatures of 165°C (1), 160°C (2), 155°C (3).

of new technologies and equipment for the production of polyamide-12 products. The proposed technique can also be used to determine the kinetic parameters of crystallization of other substances with properties similar to polyamide-12.

## CONCLUSION

The effect of the combined effects of shear stress and supercooling on the kinetics of crystallization of PA-12 is investigated.



**Fig. 3.** Dependences of the growth rate of crystal structures  $v_{\Delta}$  of PA-12 on shear rate at temperatures of 165°C (1), 160°C (2), 155°C (3).

It is shown that with an increase in shear rate, the crystallization process is significantly accelerated.

The crystallization process parameters were calculated: the induction period, the rates of nucleation and growth of crystalline structures.

The applicability of the method proposed by the authors to the description of the crystallization kinetics of PA-12 is shown when two factors are applied that affect the crystallization process.

The experimental data obtained and processed by the authors satisfactorily correlate with the known literature data and can be used in the development of new technologies and the design of equipment for the production of polyamide-12 products, as well as in existing industrial plants during commissioning or adjusting the technological parameters of extrusion processes and injection molding.

## REFERENCES

1. C. J. G. Plummer, J. E. Zanetto, P. E. Bourban, and J. A. E. Manson, "The crystallization kinetics of polyamide-12," *Colloid Polym. Sci.*, **279**, No. 4, 312–322 (2001).
2. A. Amado, K. Wegener, M. Schmid, and G. Levy, "Characterization and modeling of non-isothermal crystallization of Polyamide 12 and co-Polypropylene during the SLS process," in: *Proceedings of the 5th International Polymers & Moulds Innovations Conf.*, Ghent, Belgium, 12–14 September (2012), pp. 207–216.
3. F. Neugebauer, V. Ploshikhin, J. Ambrosy, and G. Witt, "Isothermal and non-isothermal crystallization kinetics of polyamide 12 used in laser sintering," *J. Therm. Anal. Calorim.*, **124**, 925–933 (2016).
4. Z. Meng, K. Wudy, and D. Drummer, "Crystallization kinetics of polyamide 12 during selective laser sintering," *Polymers*, **10**, No. 2, 168–182 (2018).
5. M. Liu, Q. Zhao, Y. Wang, et al., "Melting behaviors, isothermal and non-isothermal crystallization kinetics of nylon 1212," *Polymer*, **44**, No. 8, 2537–2545 (2003).
6. N. McFerran, C. Armstrong, and T. McNally, "Nonisothermal and isothermal crystallization kinetics of nylon-12," *J. Appl. Polym. Sci.*, **110**, No. 2, 1043–1058 (2008).
7. A. Ya. Malkin and A. I. Isaev, *Rheology: Conceptions, Methods, Applications* [English translation], Professiya, St. Petersburg (2007).
8. T. W. Haas and B. Maxwell, "Effects of shear stress on the crystallization of linear polyethylene and polybutene-1," *Polym. Eng. Sci.*, **9**, No. 4, 225–241 (1969).
9. Yu. A. Taran, M. K. Zakharov, A. L. Taran, and R. N. Ivanov, "Experimental determination of the rates of nucleation and growth of phase transformation centers," *Tonkie Khimicheskie Tekhnologii*, **11**, No. 6, 43–54 (2016).
10. N. Devaux, B. Monasse, J. M. Haudin, et al., "Rheoptical study of the early stages of flow enhanced crystallization in isotactic polypropylene," *Rheol. Acta*, **43**, No. 3, 210–222 (2004).
11. W. Junyang, B. Jing, Z. Yaqiong, et al., "Shear-induced enhancements of crystallization kinetics and morphological transformation for long chain branched polylactides with different branching degrees," *Sci. Rep.*, **6**, 26560 (2016).

12. C. Block, A. K. Ghosh, B. Van Mele, and G. Van Assche, "RheoDSC: Design optimisation by heat transfer modeling," *Thermochim. Acta.*, **547**, 130–140 (2012).
13. V. Janssens, C. Block, G. Van Assche, et al., "RheoDSC: design and validation of a new hybrid measurement technique," *J. Therm. Anal. Calorim.*, **98**, No. 3, 675–681 (2009).
14. B. Wunderlich, *Macromolecular Physics* [Russian translation], **2**, Mir, Moscow (1979).
15. A. L. Taran, *Powder and Melt Granulation: Theory and Practice* [in Russian], Doctoral Dissertation, MITHT, Moscow (2001).
16. Yu. A. Taran, A. V. Kozlov, and A. L. Taran, "The formation of deposits on the walls of the pores in the filtering process," *Tonkie Khimicheskie Tekhnologii*, **14**, No. 2, 15–22 (2019).
17. GOST R 56757–2015 (ISO 11357-7: 2002) *Plastics. Differential Scanning Calorimetry (DSC), Part 7. Determination of Crystallization Kinetics* [in Russian].