THE APPLICATION OF DIFFERENTIAL THERMAL ANALYSIS TO INVESTIGATION OF THERMOPLASTICS

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The courses of phenomena occurring in investigated plastics during heating were studied. The plastics specimens have been subjected to investigation before and after heating. Two kinds of plastics being applied in machine constructions Tarnamid T-27 (polyamide 6) and Tarnoform 300 (polyacetale) have been chosen to investigation.

The specimens have been subjected to heat treatment in turbine oil at minimum temperature of crystallization: polyamid 6 at 170°C and polyacetal at 140°C. It has been found that during heating in tested plastics endo- and exothermic effects take place and there are some differences for plastics before and after heating. It is possible to calculate the grade of crystallinity on the base of DTA curves. In polyamid 6, in which the polymorphic transformation takes place, the known methods of calculation of degree of crystallinity proves ineffective.

Plastics after heating characterize the higher degree of crystallinity grade.

Keywords: phase transformation, polymers, polymorphic transformation, thermoplastics

Introduction

The method of differential thermal analysis (DTA) allows to observe the heat transfer in the time or temperature dependence. The course of phenomenom was recorded as a curve showing in succession, the differences of temperature (or their absence) in investigated substance and neutral pattern substance. The DTA method is widely applied to examine the phase transformation occurring in metals and other crystalline substances [1, 2]. It is also applied in the examination of structural transformations occurring in plastics [1, 3, 4–7]. This work is the next attempt to apply the DTA method to determine the crystalline phase contents in

plastics. The aim of the work is the study of phase transformation during heating and ascertain some transformation mechanisms occurring during annealing.

Experimental

Materials tested

To test thermoplastics polyamid 6 (Tarnamid T-27) and polyacetal (Tarnoform 300) were chosen. These plastics have partially crystalline structure; they are manufactured in Poland in the form of granulated materials and are widely applied in technology. As the result of annealing, the increasing of crystalline phase and structural changes are gained. In polyamid 6 the fine-crystalline structure and in polyacetal mainly coarse-crystalline structure is formed. The structure of plastics has the essential influence on forming the physical and technological properties [6].

The part of the manufactured for testing specimens were subjected to annealing: polyamid 6 – at temperature 170°C and polyacetal – 140°C. The heating rate was 0.015 deg/s and the rate of cooling – 0.01 deg/s. The annealing were done in ultrathermostat U2C type (GDR) in turbine oil TU-20. The other specimens were subjected to the test in the row state (without annealing). The weight humidity content in the specimens of Tarnamid T-27 was 2.8–3.3% and of Tarnoform 300–0.4–0.5% by weight.

Procedure of investigations

To determine the phase transition during heating and annealing the investigation were performed before and after annealing, which enables the comparison of the results. The derivatograph Q-1500 MOM (Hungary) was used to the tests of the transformation temperatures and related heat effects. As a neutral pattern substance the aluminium oxide Al_2O_3 roasted at temperature 1000°C was used. The weighed of the fine broke up chips of plastics have been place in the crucible of the derivatograph and in the other one, the pattern substance.

The area F between the line DTA= $f(T)$ and the basic curve counted according to the formula [1] is proportional to the reaction heat ΔH [1]:

$$F = \int_{T_1}^{T_2} [\Delta T_{(T)} - \Delta T_{x(T)}] dt \qquad (1)$$

where

T_1; T_2 – temperatures of the beginning and the end of the transition,

$\Delta T_{(T)}$ – the DTA line of the tested specimen,

$\Delta T_{x(T)}$ – the basic DTA line.

The melting enthalpy of the tested substance ΔH was calculated from the relationship:

$$\Delta H = \frac{F}{m} K; \ (J / g) \tag{2}$$

where:

   F – the area of the thermogram, mm^2,

   m – the mass of the specimen, g,

   K – proportionality factor, J/mm^2

Table 1 The values of proportionality of factor K of the pattern substance

Substance	Melting temperature / °C	Melting enthalpy / $J \cdot g^{-1}$	$K/$ $J \cdot mm^{-2}$
Diphenyl	68	120.6	0.035
Naphtalene	80	148	0.036
Acenaphtene	95	120	0.051
Benzoic acid	122	141.7	0.056
Silver nitrate	212	70	0.066
Sodium nitrate	314	189.7	0.070
Potassium nitrate	337	105.9	0.071

The factor K was determined on the basis of DTA curves for several pattern substances (Table 1). Its value was calculated from the formula:

$$K = \Delta H_w \frac{m_w}{F_w}; \ (J / mm^2) \tag{3}$$

where

   ΔH_w – the melting enthalpy of the pattern substance,

   m_w – the mass of the specimen of the pattern substance,

   F_w – the thermogram area of the pattern substance.

In Fig. 1 the diagram of proportionality factor (correction factor) as a function of temperature is shown. The diagram can be approximated by the relationship (the correlation coefficient 0.97):

$$K = 9.64 \cdot 10^{-3} + 4.54 \cdot 10^{-4} T - 8.21 \cdot 10^{-7} T^2 \tag{4}$$

For the calculations of the melting enthalpy of the polyacetal ($T = 160°C$), $K = 0.061$ J/mm^2 and of the polyamid 6 ($T = 220°C$), $K = 0.069$ J/mm^2 were taken.

The calculated values of melting enthalpy ΔH were used to determine the degree of crystallinity S_k of the tested substance, from the pattern:

$$S_k = \frac{\Delta H}{\Delta H_k} \cdot 100; \quad (\%) \tag{5}$$

where ΔH_k − melting enthalpy of totally crystalline substance. The melting enthalpy of polyamide 6 with the 100% crystallinity is 187.65 J/g and polyacetal 246.0 J/g [4, 5].
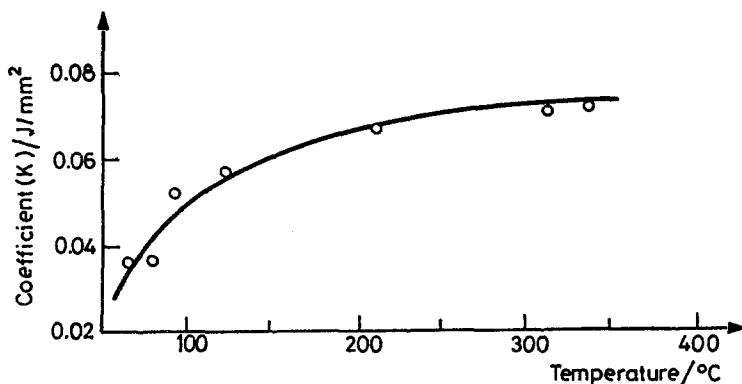

Fig. 1 The dependence of proportionality factor K on temperature

The enthalpy of transformation for tested temperature range T_1 to T_2 was calculated from a part of DTA curves area F_x for drawing the curves, which show the dependence of crystallinity grade vs. temperatures. The area of DTA curve was calculated from the formula [3]:

$$F_x = \int_{T_1}^{T_2} \Delta T \, dT \tag{6}$$

Results and discussion

The investigations by DTA method showed that in plastics the endothermic transformations mainly occurred during heating and in polyamid 6 the exothermic transformation is also to be found.

On the basis of thermoanalytical curves of polyamid 6 before annealing (Fig. 2), one exothermic effect and two endothermic ones could be determined.
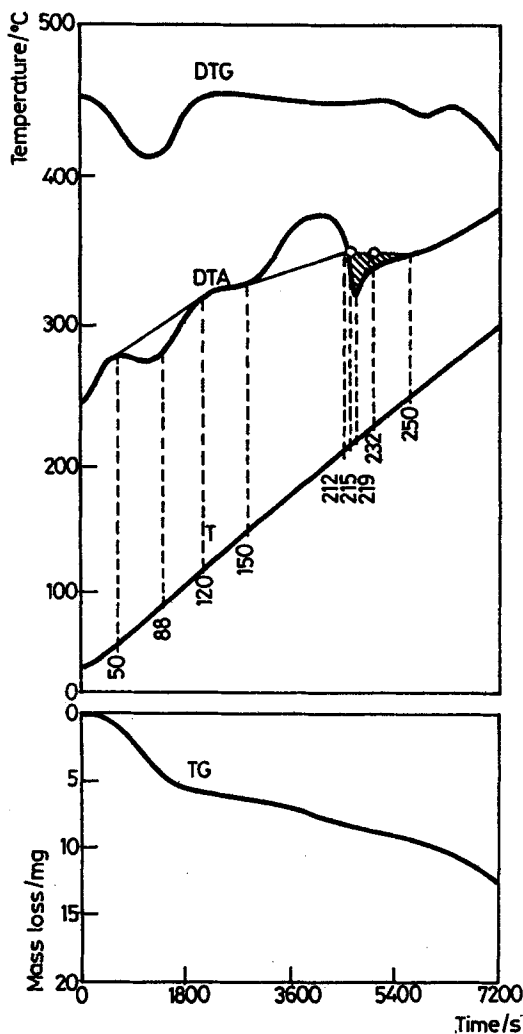
Fig. 2 The DTA curves of polyamide 6 (Tarnamid T-27) before annealing, weighed portion 200 mg, heating rate 0.0416 deg/s, test time 12000 s, temperature range 500°C (in the figure limited to 300°C), TG 50 mg, air, platinum crucible

The first endothermic effect takes place in the range of temperatures 50°–120°C. It determines the changes in plastics which are mainly connected with evaporating of water and caprolactam.

In the initial stage of heating the considerable mass loss of the specimen occurs, which illustrates the TG and DTG. It is an intensive process culminating at 85°C. At temperature higher than 100°C the mass loss is slower and it is caused mainly by evaporation of the products of partial polymer decomposition.

The mass loss of the specimens up to the melting temperature of crystalline phases is about 5.5% by weight.

The exothermic effect present in temperature range 150°–212°C determines the enthalpy of polymorphic transition and secondary crystallization before melting. Tests have been done in the atmosphere and this effect is also caused by the oxidizing the specimens. On the basis of high temperature X-ray structural analysis author [6] stated, that polymorphic transition has taken place by heating. The monoclinic crystalline α phase transforms into crystalline γ phase with the pseudohexagonal lattice, similar to the hexagonal one. Simultaneously, in the
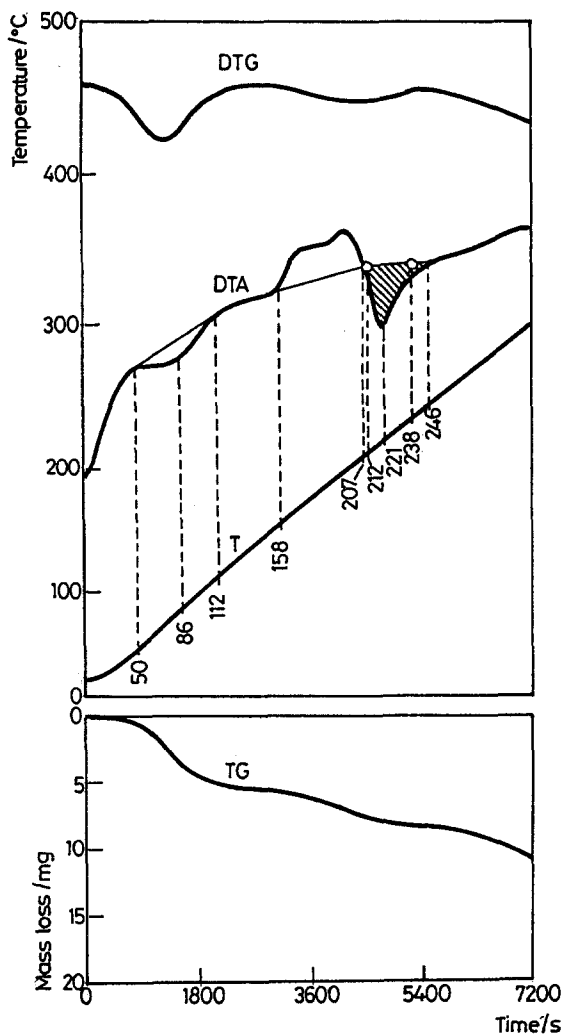

Fig. 3 The DTA curves of polyamide 6 (Tarnamid T-27) after annealing; see the test

secondary crystallization process the part of the amorphic phase transforms, into crystalline γ phase.

The second endothermic effect takes place in the temperature range 215°–250°C and determines the melting enthalpy of crystalline phases.

The thermoanalytical curves of polyamide 6 after annealing (Fig. 3) proves the similar course of phenomenon but with shifted temperature values of the detailed heat effects and their enthalpies. The annealed material characterizes smaller mass loss. The mass loss equals 3.9% by weight up to the melting temperature of the crystalline phases. The other authors' [7] investigation results show that the annealed plastics contain less water and show lower water absorbing capacity. It is caused by higher crystalline phase contents in the tested materials. This is also a reason for the lower value of the first endothermic effect. On the DTA curve of annealed plastics the considerable exothermic effect is evident.

Then, in the annealed plastics the polymorphic transition also takes place and the part of the amorphic phase transforms into crystalline phase. Because the an-
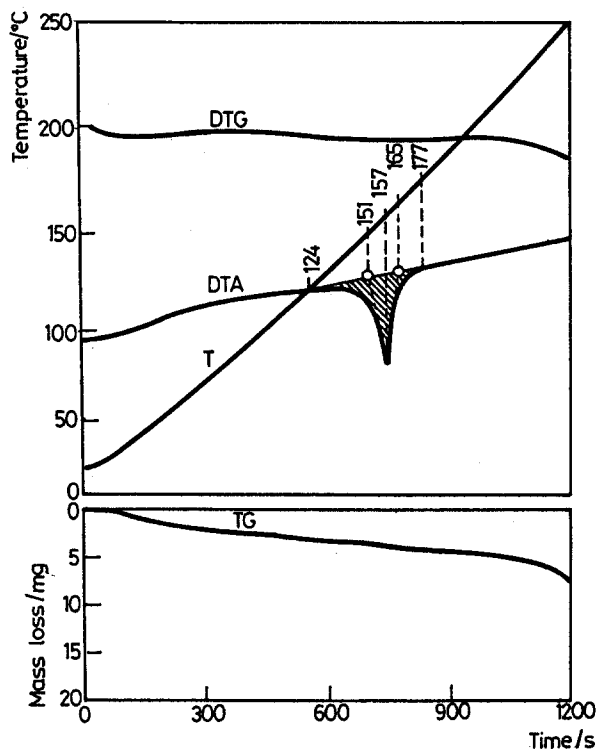

Fig. 4 The DTA curves of polyacetal (Tarnoform 300) before annealing, weighed portion 190 mg, velocity rate 0.0208 deg/s, test time 12000 s, temperature range up to 250°C,

nealed plastics contents more crystalline phase, the value of the second endother-
mic effects is higher.

The thermoanalytical curves of polyacetal before annealing presented in
Fig. 4. The large endothermic effect is qualifying the enthalpy of melting of crys-
talline phase is particularly apparent. During heating, the mass loss of the
specimen appears as well, but slower than in the specimen of polyamide 6.

The author's X-ray investigations [6] result that the polymorphic transforma-
tion does not take place in the polyacetal. The crystalline phase has the hexagonal
lattice.

The DTA curve of polyacetal after annealing is shown in Fig. 5. It shows the
shifting the start and the end of melting of crystalline phase in the direction to
higher value and higher value of enthalpy of melting. In the annealed material the
mass loss also takes place under the influence of temperature. It is to assume that
the material with higher share of crystalline phase is more temperature resistant.
On the basis of DTA curves of the tested plastics the degree of crystallinity was
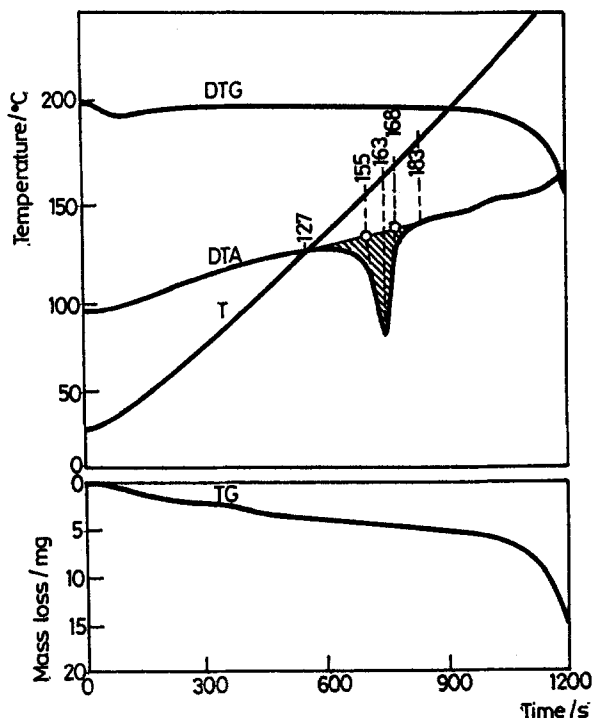calculated.

Fig. 5 The DTA curves of polyacetal (Tarnoform 300) after annealing; see the test parameters
in Fig. 4

On the basis of thermograms the melting enthalpy and crystalline degree were calculated. The melting enthalpy of polyamid 6 before annealing is 37.4 J/g and after annealing 58 J/g.

The dependence of crystalline degree from temperature of heating is shown in Fig. 6. From the course of curves shown in the figure you can observe that the degree of crystallinity of plastics before annealing is 19.8% and the annealed one is 30.9%.

These values are considerably smaller that the ones which has been gathered by the author in X-ray method (67.1% and 78.3% respectively [7]).
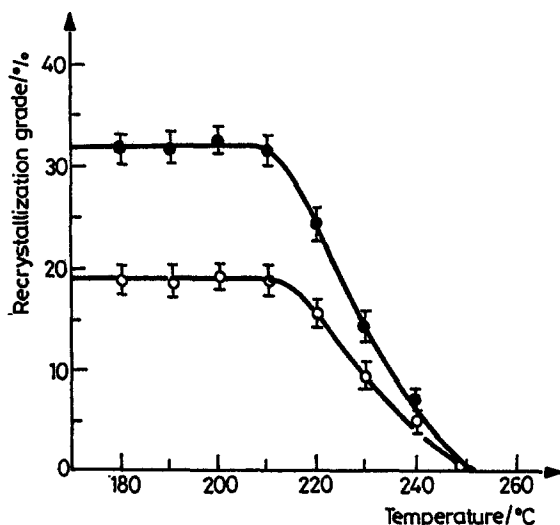

Fig. 6 The dependence of degree of crystallinity of polyamide 6 (Tarnamid T-27) vs. heating temperature. o – Tarnamid T-27 before annealing; ● – Tarnamid T-27 after annealing

To prove the rightness of calculations of crystallinity the additional examination on the polyamide 6 have been done by DSC method, in atmosphere of nitrogen (30 cm^3/min) vs. time of heating. The DuPont 990 Thermal Analyser equipped with Standard DSC CEll was used. The mass of specimen was 8 mg and the heating velocity was 10 deg/min; the covered aluminium container was compared with basis aluminium one.

The specimens were heated from room temperature; at the temperature 150°C the registration of thermoanalytical curves vs. time was switched on.

The registered DSC curves, presented in Fig. 7 showed only the enthalpy of melting and are destined to exact determination of this enthalpy.

The melting enthalpy was calculated from the formula:

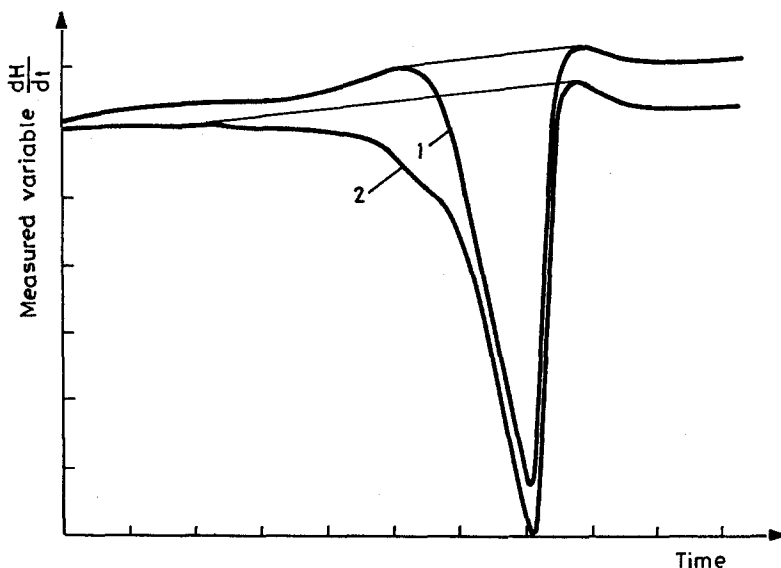$$\Delta H = 4.187 \frac{A}{m} B \, E \, Y; \quad (J / g) \tag{7}$$

Fig. 7 The DSC curves of polyamide 6 (Tarnamid T-27) done in nitrogen: (1) the material before annealing, (2) the material after annealing

where:

A – area of the DSC curve, mm^2,

m – the mass of the specimen, mg,

B – the time base of recording, 0.0394 min/mm,

E – the calibration coefficient, equal 1,

Y – the amplification of the signal, equal 0.4722 mcal/min·mm

The determined melting enthalpy (40.1 and 54.6 J/g) allowed to calculate the crystallinity, which is 21.4% for polyamid 6 before heat treatment and 29.1% for the polyamid subjected to heat treatment. These values are comparable with the one by DTA method.

Then, it could be stated that both DTA and DSC method gave for polyamid 6 considerable lower values of crystallinity of the ones by X-ray method. The author does not recommend these methods for determining the degree of crystallinity of polyamid 6 because in this plastics the polymorphic transition during heating influences the decrease of registered melting enthalpy. There is no information in literature on this subject. There is only an opinion that the exact determination of melting enthalpy is impossible for plastics in which polymorphic transition occurs [1].

The melting enthalpy of the polyacetal before annealing is 147 J/g, and after annealing 176.5 J/g. The crystalline degree accordingly 59.7% and 71.7%. In this material the polymorphic transition does not occur; then the crystallinity counted

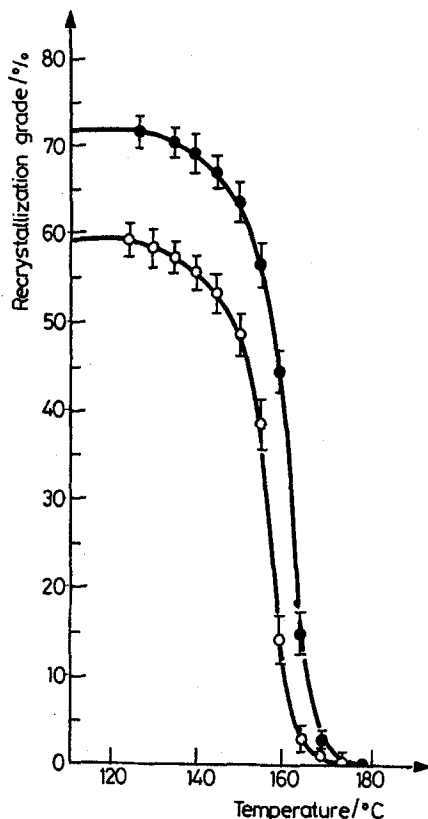on the base of melting enthalpy is comparable with the value obtained by the author in X-ray method [6].

Fig. 8 The dependence of degree of crystallinity of polyacetal (Tarnoform 300) *vs.* heating temperature . o – Tarnoform 300 before annealing; ● – Tarnoform 300 after annealing

On the Fig. 8 the dependence of the degree of crystallinity *vs.* heating temperature of polyacetal is shown. The course of the degree of crystallinity in the function of heating temperature is similar to the one of polyamide 6, but the degree of crystallinity decreases in the moment when melting of crystallinity phases starts.

The annealed plastics characterizes the higher value of the temperature determining the end melting effect.

The statistical analysis of the results showed there are essential differences between the values of crystallinity at various temperatures for plastics before and after annealing.

Conclusions

During heating of polyamide 6 and polyacetal, the phase transition connected with endo- and exothermic effects takes place. Also, the transition of crystalline phases into morphic ones, mass loss, density decrement and polymorphic transformation in polyamide 6 (Tarnamid T-27) results.

The increase of melting enthalpy of crystalline phases and shifting of temperature range of this effect for the annealed plastics testifies that during annealing the increase of share of crystalline phase and the value of crystallinity is higher.

The annealing should be realized in the temperature in which the highest secondary crystallization takes place. To obtain the considerable growth of crystalline phase, the process must last enough to enable the regrouping of the macromolecules.

The annealing of specimens of polyamide 6, done in temperature of 170°C in which the polymorphic transformation and secondary crystallization takes place as the DTA curves show. The annealing of polyacetal is realized at temperature of 140°C where the melting of crystalline phase starts.

As a result of the delivered energy, the activity of macromolecules increases and the new crystal nucleus creates.

As a result of secondary crystallization the growth of existing crystalline structures follows through linking the amorphic phase macromolecules, whereas the elements of crystalline structure creates simultaneously.

The findings allow to express the conclusions as follows:

– heating causes the change of phase composition on investigated plastics and gradual decrease of crystalline phase to zero at melting temperature when in polyamide 6 (Tarnamid T-27) still polymorphic transformation takes place,

– during annealing, through secondary crystallization the increase of crystalline phase process,

– it is not recommended to apply the DTA or DSC method for calculation of crystallinity grade of polyamide 6 (Tarnamid T-27), (during heating of this plastics the polymorphic transition proceeds) because the results are considerably lower than the ones by X-ray method.

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Zusammenfassung — Es wird untersucht, welche Erscheinungen beim Erhitzen von zwei im Maschinenbau verwendeten Plasten, d.h. von Tarnamid T-27 (Polyamid 6) und von Tarnoform 300 (Polyacetal) auftreten und wie sich die Wärmebehandlung auf die Eigenschaften der untersuchten Plaste auswirkt.

Die Proben wurden in Turbinenöl auf die Mindest-Kristallisationstemperatur erhitzt: bei Polyamid 6 auf 170°C, bei Polyacetal auf 140°C. Man fand, daß beim Erhitzen in den untersuchten Plasten einige endo- und exotherm Effekte auftreten und daß einige Unterschiede zwischen Plasten vor und nach der Wärmebehandlung bestehen. Anhand der DTA-Kurven kann der Kristallinitätsgrad berechnet werden. In Polyamid 6, wo polymorphe Umwandlungen stattfinden, erwiesen sich die bekannten Methoden zur Berechnung des Kristallinitätsgrades als uneffektiv.

Die Plaste werden nach der Wärmebehandlung durch einen höheren Kristallinitätsgrad gekennzeichnet.