Crystallization kinetics of polycaprolactone in nanocomposites

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Abstract: The paper presents research results on the crystallization kinetics of polycaprolactone (PCL) with micro- and nano-additives such as talc (nucleation agent) and nanosilver (antibacterial agent). The process of isothermal crystallization was studied in a narrow temperature range 38.5—41.5 °C using Differential Scanning Calorimetry (DSC) and Thermooptical Analysis (TOA) methods. The kinetics of the process are described using the Avrami model. The parameters *n* and log *K* of the equation were calculated. Changes in the half time of crystallization, degree of crystallinity and melting temperature of the polymer under the influence of the fillers and the conditions of crystallization were analyzed.

Keywords: crystallization, polycaprolactone, nanosilver, talc, nanocomposites.

Kinetyka krystalizacji polikaprolaktonu w nanokompozytach

Streszczenie: Przedstawiono wyniki badań kinetyki krystalizacji polikaprolaktonu z mikro- oraz nanododatkami, takimi jak talk (czynnik nukleacji) i nanosrebro (dodatek antybakteryjny). Metodami różnicowej kalorymetrii skaningowej (DSC) oraz analizy termooptycznej (TOA) badano proces krystalizacji w zakresie temperatury 38,5—41,5 °C. Kinetykę procesu opisano za pomocą modelu Avramiego. Wyznaczono parametry *n* oraz log *K*. Przeanalizowano wpływ dodatku napełniaczy i warunków prowadzenia procesu krystalizacji na zmiany połówkowego czasu krystalizacji, temperatury topnienia oraz stopnia krystaliczności polimeru.

Słowa kluczowe: krystalizacja, polikaprolakton, nanosrebro, talk, nanokompozyty.

Polycaprolactone (PCL), as an aliphatic polyester, has received much attention because of its' possible application as both a biocompatible and biodegradable material. For biomedical purposes, PCL may be used in drug delivery systems or tissue engineering scaffolds [1—3]. Thus the crystallization process and the morphological properties of PCL are important. PCL is a semicrystalline polymer and its final properties depend on the crystalline fraction, which is affected by the conditions of crystallization. The study of the crystallization kinetics of PCL has also considerable practical significance.

Isothermal and nonisothermal (dynamic) studies of PCL crystallization were reported in the literature [4—6]. For the investigation of polymer crystal nucleation and growth, conventional techniques such as DSC cannot cool fast enough to prevent nucleation of the rapidly crystallizing polymer. The first extensive research [4] on PCL crystallization using DFSC (Differential Fast Scanning Calorimetry) traces demonstrated the enormous capabilities of this new calorimetric technique with the possibility of very fast cooling to avoid any nucleation. According to the authors [4], the crystallization of PCL could be connected through two basic stages. At first, a homogeneous (or heterogeneous) nucleation at a given temperature was considered to be initiated as soon as a critical free energy barrier was overcome. Following nucleation, a growth of small to large crystals depended on temperature. Further growth of the initial crystals was hindered by slow, long-range diffusion.

In the other published paper [5], the authors applied the Avrami model to DSC experimental results on PCL crystallization. DSC crystallization curves in integral forms were fitted to simulated Avrami curves. The experimental curves show deviations from the model in later stages of polymer crystallization.

In another paper [6], from a comparison of viscoelastic, calorimetric, and optical observations, it was found that the viscoelastic properties start to improve at a relatively high degree of crystallinity and when the crystalline structures are very much developed. These facts, together with morphological observations, suggest that the microstructure at the gel point is governed by the interactions between growing crystallites.

Screening new materials for use in different areas of industries resulted in the development of novel poly-

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meric materials. Nano- and micro-particles provide new application opportunities for plastic materials with improved properties. The presence of the additive can influence the physical, chemical and mechanical properties of the polymer/nano- or micro-filler material. Over the past decade, aliphatic polyesters, such as polycaprolactone (PCL) in composites (also with nanosilver) have been intensively studied [7—12].

The authors [10] studied the isothermal crystallization of PCL with polycaprolactone/clay nanocomposites containing different clay concentrations. They showed that the well-dispersed organoclay platelets act as nucleating agents in the PCL matrix, reducing the crystallization half time $t_{1/2}$. The Avrami equation was able to describe the isothermal crystallization of neat PCL and PCL/clay nanocomposites up to a critical value of the relative crystallinity, where deviation from the model was observed. This critical value was reduced by the presence of nanoclay.

Additionally, the effect of γ radiation on the crystallization of PCL has been studied [13]. The morphological structure of PCL crystallization in thin films is discussed in another paper [14].

In the presented work, the PCL crystallization process in PCL/Ag nanocomposites was studied under isothermal conditions in a narrow range of temperatures. Additionally, the crystallization of PCL in PCL/talc composites was discussed. The Avrami equation was chosen to discuss the influence of the additives on the rate of PCL crystallization in the composites.

Talc, known to be a nucleation agent, is used for comparison with silver particles effecting the crystallization kinetics of PCL.

EXPERIMENTAL PART

Materials

Polycaprolactone (PCL) with molecular weight M_n = 70.000—90.000 and melting point of 60 °C was purchased from Sigma-Aldrich. Additives included: pharmaceutical talc [$Mg_3Si_4O_{10}(OH)_2$] of the Polish Pharmaceutical Aflofarm (microsize particles) and organically modified nanosilver (particle size <100 nm) from Sigma-Aldrich.

Preparation of samples

Composite samples were obtained by short melt mixing using a mechanical stirrer for PCL and filler in a weight ratio of 100:1 in a vessel at 100 °C. In order to obtain thin films (d = 15 μm), composite samples were pressed under 8 MPa in a hydraulic press with a hot stage at 70 °C.

Methods of testing

— To investigate the crystallization kinetics and degree of crystallinity of pure PCL and PCL in nano- and microcomposites, a Mettler Toledo FP90 DSC calorimeter with a FP85 measuring cell was used. The sample mass in the DSC study was close to 9 mg. Before the experiment, calibration with Indium Standard (melting point 156.6 °C) was made.

The DSC analysis was carried out in the following stages. Initially, a sample was heated from room temperature T_1 to T_2 = 80 °C, incubating 10 minutes to completely destroy any initial crystalline structure of the polymer. Next, the sample was cooled at 50 °C/min to the crystallization temperature T_c. The isothermal crystallization was carried out for 1 h in a narrow range of temperatures, 38.5—41.5 °C. In the next stage, the sample was heated with a heating rate equal to β = 10 °C/min to measure the melting temperature T_m of the sample after crystallization. Figure 1 shows the schematic diagram of the DSC stages in the experiment.

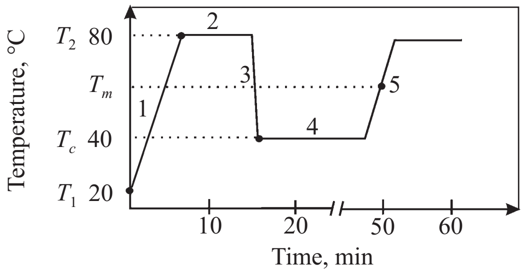

Fig. 1. Schematic diagram of DSC stages, temperature — time profile: 1 — heating from T_1 to T_2 (~6 min), 2 — heating at T_2 (~10 min), 3 — cooling from T_2 to crystallization temperature T_c (~2 min), 4 — crystallization (time 35 min), 5 — heating from T_c to T_2 (~4 min); T_m — melting temperature

— For the thermooptical analysis (TOA), a Mettler Toledo FP90 DSC calorimeter with FP82 thermooptical cell and polarizing microscope was used. The crystallization in the TOA analysis was carried out under isothermal conditions (the same as in DSC). The thermooptical curves of crystallization kinetics (for pure PCL and PCL in the composites) describing the relative light intensity in cross polarizers (I/I_0) versus time were drawn.

RESULTS AND DISCUSSION

Analysis of isothermal crystallization kinetics

The kinetics of isothermal crystallization can be described by the Avrami model [15].

In order to determine the n and K parameters, the Avrami equation (1) is presented and drawn in the logarithmic form (2). From the slope and intercept of the linear dependence of the left side of the equation (2), the log t, n and K parameters can be found.

$$1 - X_t = \exp(-K \cdot t^n) \qquad (1)$$

$$\log[-\ln(1 - X_t)] = n \cdot \log t + \log K \qquad (2)$$

where: X_t — relative degree of crystallinity, n — time parameter determining the dimension of the crystallization process, K — parameter dependent on the nucleation rate.

The above equation was based on some simplifications that do not necessarily apply to the crystallization of macromolecules [16] in which: volume does not stay constant on crystallization, number of nuclei may not increase continuously, linear growth is not constant with time, crystal morphology is not spherical, where crystalline substructure branches occur, there can be two stages of crystallization, and changes of crystal perfection is observed.

Two steps in the spherical crystallization as a complication of the overall crystallization rate have been considered by Price [17] as follows. After the spherulite boundary has passed a particular point of time, a second crystallization step is assumed to be initiated also following an Avrami type expression but with a parameter close to $n_2 = 1$ (fibrilar type).

Thus initial crystallinity is described by the following equation (3):

$$1 - X_t = \exp\left(-K_1 \cdot t^{n_1}\right) \qquad (3)$$

where: n_1 being either 3 or 4, depending on the type of nuclei.

This is followed from time τ by the secondary process described by the following equation (4):

$$(1 - X_t) = \exp\left[-K_2(t - \tau)^{n_2}\right] \qquad (4)$$

where $n_2 \approx 1$.

Other authors [18] present the concept in which the secondary crystallization is hindered by the non-crystallizable part of the macromolecules, loops and entanglements but an increase of crystal perfection leads in consequence to a gradual reduction of the surface to volume ratio by fold-length growth. The experimental evidence for an increase of crystal perfection during crystallization was presented by Wunderlich [16].

Thus, there is a large range of effects that may alter the classical Avrami assumption.

The Avrami equation is usually only valid [16] at low conversions as long as the impingement in not serious. Experimentally, the Avrami equation and parameters are a convenient way to represent the empirical data of crystallization.

DSC results of isothermal crystallization

Analysis of the thermograms of isothermal crystallization of pure PCL and PCL in the composites showed a significant influence of nanosilver and talc on its crystallization kinetics. The PCL crystallization time in the composites was significantly reduced compared to pure polymer. The induction time was equal to a few minutes. Both additives are thus nucleating agents of PCL.

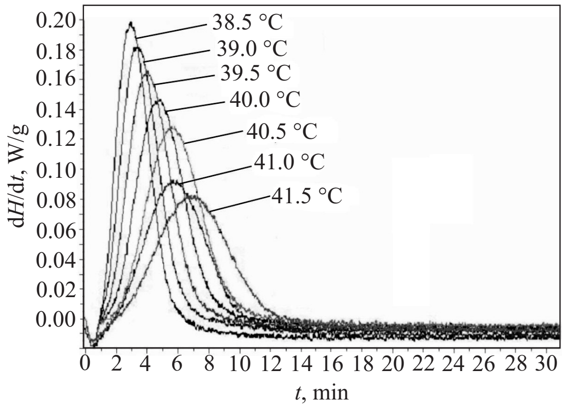

Fig. 2. DSC crystallization thermograms (heat flow d*H*/d*t* of crystallization versus time) of PCL in the composite with nanosilver drawn in a narrow crystallization temperature range 38.5—41.5 °C

Figure 2 shows an example of the experimental DSC thermogram describing the crystallization heat flow versus time in the process of isothermal crystallization of PCL in the composite with nanosilver in a narrow range of crystallization temperatures from 38.5 to 41.5 °C.

DSC thermograms allowed the determination of the relative crystallinity degree using equation (5):

$$X_t = \frac{\int_0^t \left(\frac{\mathrm{d}H_c}{\mathrm{d}t}\right) \cdot \mathrm{d}t}{\int_0^\infty \left(\frac{\mathrm{d}H_c}{\mathrm{d}t}\right) \cdot \mathrm{d}t} \cdot 100\ \% \qquad (5)$$

where: X_t — relative crystallinity degree (variable in time), $\mathrm{d}H_c$ — differential crystallization heat, t — time.

Integral curves showing the dependence of the degree of crystallinity X_t, normalized to 100 % versus time can be plotted.

Figure 3 shows the integral curves of crystallization at various temperatures of pure PCL and PCL in the composites with nanosilver and talc, respectively.

Figure 4 shows the Avrami plots in the logarithmic form [equation (2)].

The Avrami model was well fitted [equation (2)] in a range of two linear plots (of two steps) drawn for lower and higher crystallization times (Fig. 4 b, c). From the slopes the time exponent n (n_1 and n_2) and from the value of intercepts, the parameter log K was obtained.

As the crystallization proceeds and neighboring crystallites begin to impinge, the crystallization will deviate from the Avrami expression and show a slower growth rate. The impingement is more pronounced in the case of PCL crystallization in the composites. No distinct second stage is observed for pure PCL in the narrow range of crystallization temperature under study. Similar values of the n parameter equal to 3—4 is found in the literature [19], which depends on the molecular weight of the PCL samples and temperature of crystallization. Others authors [20] found a change in growth rate coupled to the change in morphology from nospherulite to spherulite forms for low molecular weight PCL. The calculated

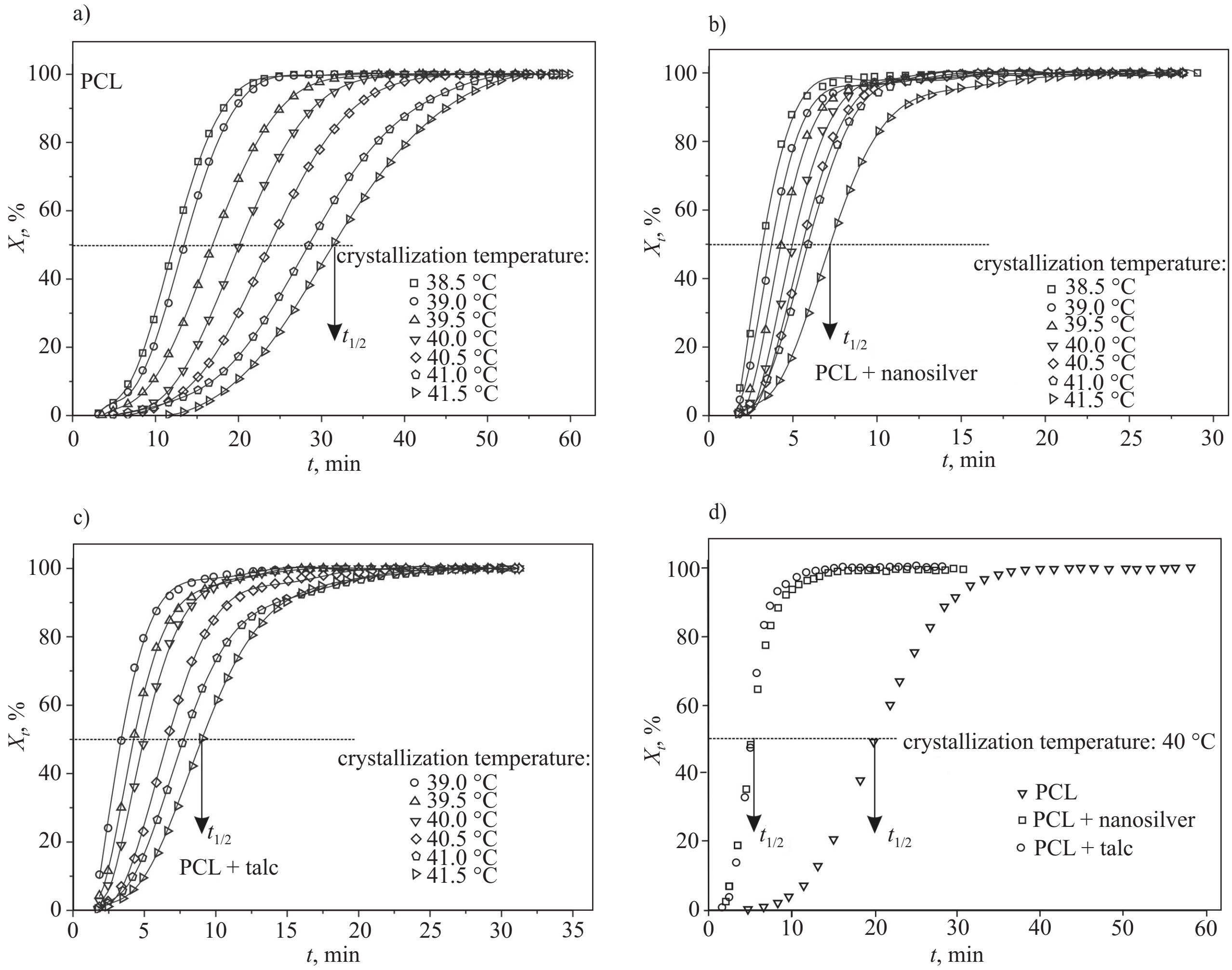

Fig. 3. Integral curves of crystallization of: a) PCL, b) PCL + nanosilver, c) PCL + talc as a function of crystallization temperatures, d) pure PCL and doped PCL for comparison at a fixed value of T_c = 40 °C

T a b l e 1. Crystallization parameters obtained for PCL and PCL composites

T_c, °C	PCL			PCL + nanosilver				PCL + talc			
	n	$t_{1/2}$, min	$(t_{1/2})_c$, min	n_1	n_2	$t_{1/2}$, min	$(t_{1/2})_c$, min	n_1	n_2	$t_{1/2}$, min	$(t_{1/2})_c$, min
38.5	3.14	12.55	12.18	2.83	0.75	3.50	3.23	2.71	0.89	3.68	3.24
39.0	3.24	13.68	13.33	3.12	1.04	4.00	3.60	2.32	1.01	3.68	3.42
39.5	3.14	17.28	16.75	3.63	1.15	4.52	4.38	2.81	1.27	4.55	4.20
40.0	3.55	20.57	20.00	3.98	1.41	5.11	5.02	3.02	1.51	5.13	5.02
40.5	3.49	24.21	24.00	3.49	1.52	5.89	5.67	3.28	1.32	6.65	6.83
41.0	3.11	24.89	28.57	4.12	1.47	5.57	5.93	3.05	1.42	7.74	7.88
41.5	3.86	29.66	31.62	3.47	1.48	7.12	7.22	3.30	1.45	8.78	8.95
	3.36 average			3.52 average	1.26 average			2.93 average	1.26 average		

n — value of Avrami parameter, n_1 — first step, n_2 — above $t_{1/2}$, $t_{1/2}$ — second step of crystallization, $(t_{1/2})_c$ — calculated (Eq. 6) half time of crystallization.

parameters for n are given in Table 1, log K parameter is drawn in Fig. 5.

The observed changes in the straight line slopes presented in Fig. 4, and thus the value of parameter n after some time of crystallization, indicate the difference in the mechanism of nucleation and the shape structure of the growing crystallites. This can be connected with growth restriction due to crystal structures of a higher rigidity as well as possible interactions between growing crystallites. Values of n close to 3 correspond to athermal nucleation (simultaneously formed nucleus) and three dimensional growth. A decrease in the n parameter value in the later time of crystallization to 1—1.3 indicates a change in both the type of nucleation (secondary nucleation) and

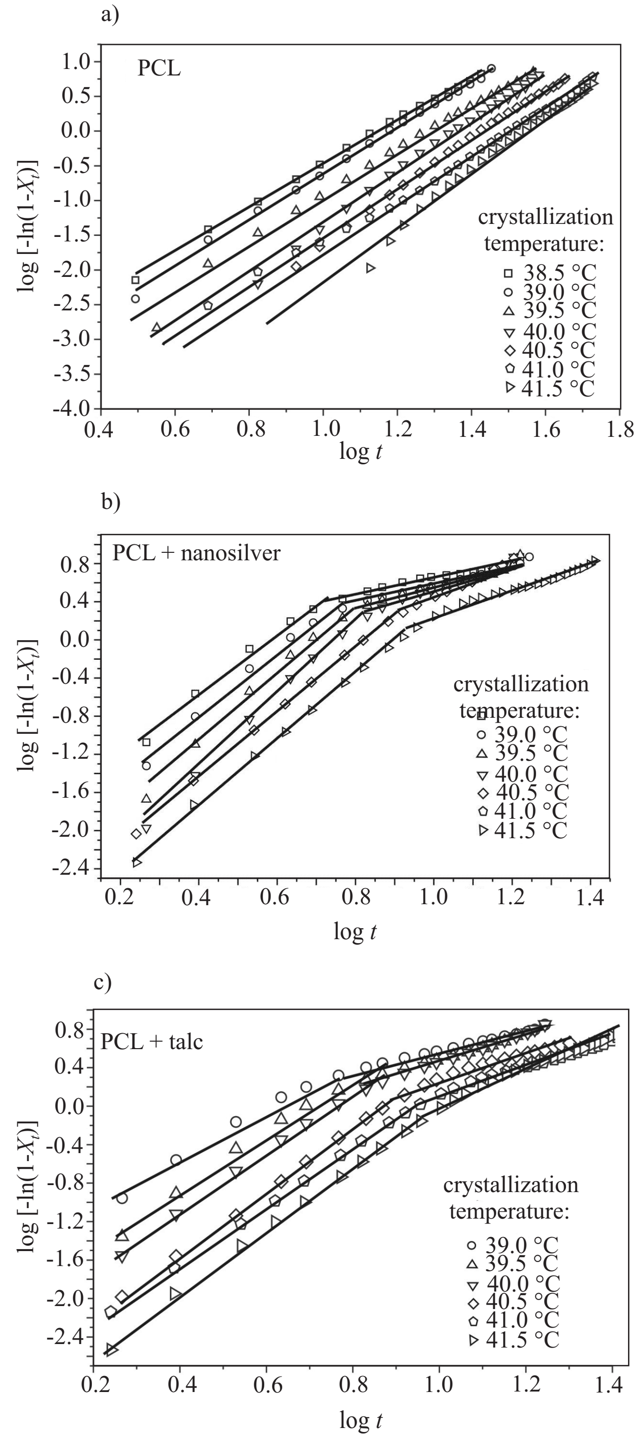

Fig. 4. Avrami curves for: a) PCL, b) PCL + nanosilver, c) PCL + talc; average coefficient of determination for linear plots R^2 = 0.97—0.98

the morphology of the growing crystallites. Figure 5 shows the dependence of log *K* (reflecting the rate of nucleation — primary and secondary) for early and late steps of crystallization versus crystallization temperature under study. The parameter *K* (log *K*) decreases with higher crystallization temperatures but also it increases in the presence of additives Ag and talc.

Based on the analysis of integral crystallization curves (in the temperature range 38.5—41.5 °C), the crystallization half-time $t_{1/2}$ was determined. The half-time of crystallization was determined for pure PCL and the composites. $t_{1/2}$ was measured as the time needed for reaching 50 % relative degree of crystallinity (see, for example, Fig. 3).

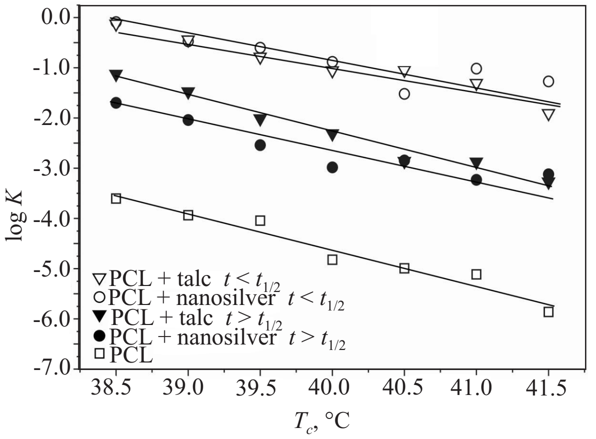

Fig. 5. Dependence of log *K* on crystallization temperature T_c

Figure 6 shows the dependence of crystallization half-time $t_{1/2}$ on the crystallization temperature T_c.

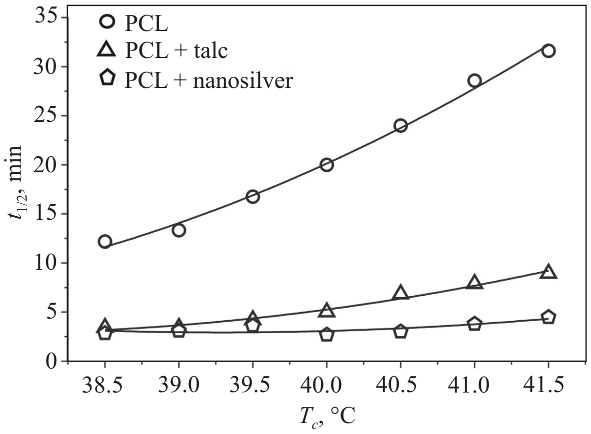

Fig. 6. Dependence of crystallization half-time $t_{1/2}$ on the crystallization temperature T_c

A decrease in the crystallization half-time of PCL in the composites is clearly observed.

The half time of crystallization $t_{1/2}$ is a property related to the rate constant. If the crystallization follows the Avrami expression, the half-time can be deduced from equation (6):

$$t_{1/2} = \left(\frac{\ln 2}{K}\right)^{\frac{1}{n}} \qquad (6)$$

In Table 1, the half-time values calculated from equation (6) are compared with those obtained from the experimental data and thus independent of the crystallization model. The values for all samples were found to be in good agreement. The half time values may be understood as a function of two competing processes — nucleation and molecular mobility. The $t_{1/2}$ values increase in general with molecular weight [17].

Melting studies

After the isothermal crystallization process, the samples were directly analyzed by heating (10°/min) in a DSC apparatus (stage 5 — Fig. 1).

The crystallinity degree of the samples after the crystallization process at T_c temperatures was determined from DSC melting curves (peak T_m) by equation (7):

$$X = \frac{\int_{T_0}^{T_\infty} \left(\frac{\mathrm{d}H_m}{\mathrm{d}T} \right) \cdot \mathrm{d}T}{\Delta H_c} \cdot 100\ \% \tag{7}$$

where: $\mathrm{d}H_m$ — heat of melting, $\Delta H_c = 139.5$ J/g — heat of fusion of 100 % crystalline PCL [9], T_0 and T_∞ — temperatures of onset and end of melting.

Analysis of the DSC melting thermograms (not shown) of these samples (PCL and PCL in composites) shows that:

— the determined crystallinity degree X of PCL crystallized in a narrow temperature range 38.5—41.5 °C is quite low and slightly lower in the nanocomposites. X for pure PCL ranged from 24.7—31.1 %, for the composite PCL + talc equaled 22.6—28.4 %, PCL + silver equaled 20.7—26.7 % depending on the crystallization temperature.

— The presence of additives causes an increase of T_m of polycaprolactone by several degrees. The additives behave as reinforcing substances leading to the increase of T_m of PCL (antyplasticizing effect). Figure 7 shows the dependence of the melting temperature T_m (peak) on the crystallization temperature T_c.

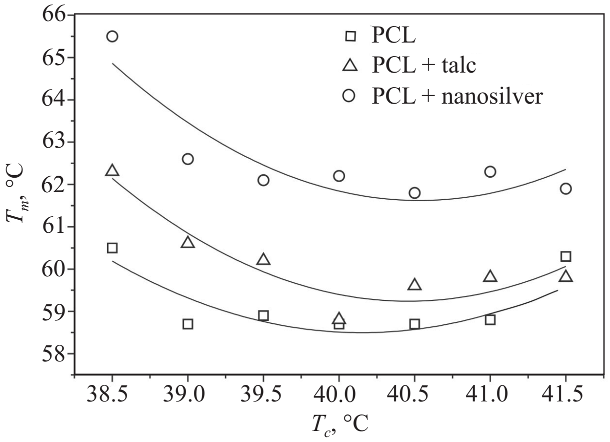

Fig. 7. Dependence of the melting temperature T_m (peak) on the crystallization temperature T_c

The nature of the curves in Fig. 7 is atypical (T_m most often increases with T_c) indicating structural reorganization during heating of the samples (in the DSC apparatus) previously crystallized at lower (than 40 °C) temperatures. This leads to an observed increase of T_m (increase of crystal perfection) by about 2—3 °C.

Observation of PCL crystallization in thermooptical analysis (TOA)

Figure 8 shows examples of the thermooptical curves and low magnification (in crossed polarizers) microphotographs of the PCL crystalline structure, pure and in the composites, occurring during crystallization at 40 °C. The curves describe changes in relative light intensity passing through the crystallizing sample as a function of time. This reflects changes in the molecular order. The behavior confirms the DSC data of a two stage process of crystallization (Fig. 3).

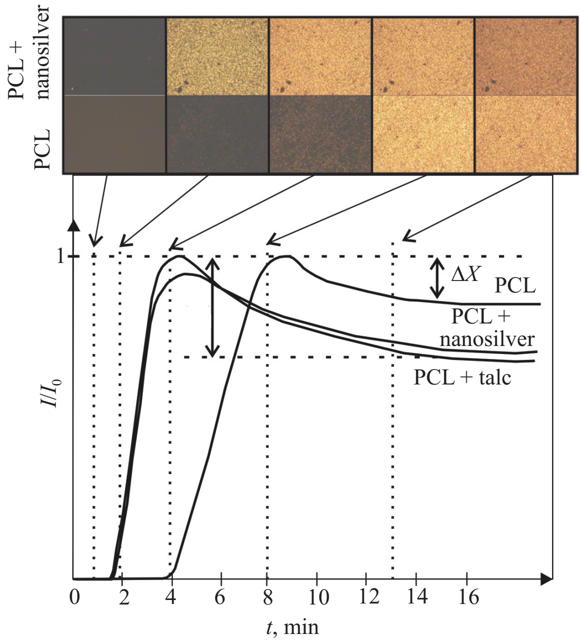

Fig. 8. Thermooptical curves presenting relative light intensity I/I_0 versus time obtained for PCL and PCL in the composites at crystallization temperatures equal to 40 °C together with microphotographs (in polarized light) of the formed crystalline structures; Δx — degree of darkening — second step of crystallization (thickening of crystals)

It is observed for the PCL composites with nanosilver:

— shorter induction time of crystallization;

— faster change (greater slope) of I/I_0 in the time of crystallization — increasing rate of crystallization;

— much larger decrease I/I_0 in late step of crystallization, which indicates a change in the morphology of the growing crystallites and the type of nucleation; thickening of crystals leads to darkening of the microscopic image in the late step of crystallization (Δx), which is lighter for pure PCL;

— The crystallization of PCL in the composites with Ag and talc run similarly; both Ag and talc are nucleating agents of PCL crystallization.

The microphotographs of chosen samples (made in crossed polarizers) show the change of field brightness occurs during primary and secondary (determined by thickening of crystalline structures) crystallization.

CONCLUSIONS

The crystallization studies of PCL in the composites using calorimetric and thermooptical analyses indicate the complexity of the process [5]. However, it can be described using the Avrami equation fitting well the early step of crystallization and also following the second step of secondary crystallization.

The determined half-time crystallization and the value of the n parameter equal to 3—3.5 confirms the three-dimensional, athermal crystallization nucleated by some possible impurities in the PCL and by the presence of the additives of nano (silver) and micro (talc) size in the composites. A further growth of crystals ($n \sim 1—1.5$) due to thickening of crystals takes place on the surface structures following the secondary nucleation. The low value of crystallinity degree of the samples, following the crystallization regime under study, indicates that the process appears incomplete. This is happening slowly due to structural limitations (impingements).

The presence of Ag and talc leads to an increase of both the melting temperature of PCL and the growth rate of nucleation (log K) and to changes in the structure of the PCL. These agents cause a broad modification of the physical properties of the polymer. Similar behavior was observed also in a case of PCL modified by intercalated and exfoliated clay minerals [20].

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