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Study of the effect of modified montmorillonite as a filler on the properties of composite granules based on polycaprolactone

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The paper presents the results of a study of the effects of the „Monament-101“ filler and the method of obtaining on the properties of composite granules based on polycaprolactone (PCL). DSC and X-ray diffraction analysis showed an increase in the degree of crystallinity from 52 to 67% and a slight decrease in the melting point (by 2°C) as the clay was introduced into the polymer.

Keywords: polycaprolactone, montmorillonite, composites, crystallinity, melting point.

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Polycaprolactone (PCL) is a biodegradable polyester synthesizable from ε-caprolactone; due to its physical properties and commercial availability, it is a polymer quite suitable for packaging industry, agriculture, and other applications [1]. To improve its performance and accelerate biodegradation, PCL is often studied in combination with the following polymers: poly-3-hydroxybutyrate [2], polyactide [3], starch [4] and inorganic fillers [5,6]. One of the most often used types of fillers for PCL is montmorillonite. Inclusion of the clay micro— or nano-particles ambiguously affects the crystallinity, size, shape and morphology of crystals and/or crystallization kinetics of the pure polymer matrix. For instance, work [7] has proved that adding clays of different types (unmodified MMT and Cloisite 30B) (2.5%) into the PCL polymer matrix causes a reduction of the composite crystallinity from 52 to 41% in case of adding MMT and increase to 53% in case of Cloisite 30B. In [8], crystallinity of the PCL composites obtained by hot extrusion depended on the added clay type (Cloisite 30B, Nanofil 804, Pangel S9) and increased from 47 to 53%. In [9], adding of clay Cloisite Na$^+$ (CNa) and Cloisite 10A (C10A) into PCL films caused an increase in the sample crystallinity from 52 to 55%. In [10], crystallinity of the PCL−Cloisite 30B and PCL−MCM-41 composites obtained by extrusion changed insignificantly (from 45.7 to 46.8%). Adding clay to the polymer matrix can potentially result in obtaining materials with structures of three different types: separate-phase composites, intercalated composites and exfoliated composites.

The goal of this work was to study the filler effect on the properties of composite granules based on polycaprolactone depending on the granule fabrication procedure. As a filler for the PCL-based polymer matrix, „Monament-101“was used, which is a highly purified montmorillonite organo-modified with alkyl-dimethyl-ammonium chloride (CJSC „METACLAY“, Bryansk Region, Russia). Unlike the published studies, in this work the influence of the composite granules fabrication procedure on their characteristics, namely, the melting point and degree of crystallinity, was investigated in addition to the influence of the very fact of filler inclusion. For this purpose, two radically different techniques were used: fabricating the granules from solution and by extrusion from melt.

In this study we used biodegradable polymer PLC produced by Sigma Aldrich (USA) with the weight-average molecular mass $M_w = 80\,\mathrm{kDa}$, crystallinity $C_x = 52\%$, melting point $T_m = 57^\circ\mathrm{C}$. As a solvent, chloroform (CH) (Ekos-1, Russia) was used. When the „from-solution“technique was used, the granules were obtained from the mixtures of polycaprolactone with filler „Monament-101“, PCL being pre-dissolved in chloroform (3% solution). After that, „Monament-101“was introduced into the prepared solution in the following concentrations: 5, 10, 25 and 50% of the polymer weight. The obtained mixture was agitated in a magnetic shaker for 24 h at 3000 rpm. Then the mixture was drawn up into a syringe, squeezed out so as to form a filament, and the filament was left for drying in an exhaust hood. After that, the filament was cut into granules. From the melt, granules consisting of PCL and „Monament-101“ were fabricated with extruder Brabender GmbH (Germany) at the melting point of 90°C. The polymer was premixed with clay in the measurement mixer Brabender 50 EHT (Germany) in the same proportions as in the solution technology. During the analysis, the prepared samples were designated as follows: S_PCL/M 5%, S_PCL/M 10%, S_PCL/M 25%, S_PCL/M 50% — for the samples fabricated from solution; E_PCL/M 5%, E_PCL/M 10%, E_PCL/M 25%, E_PCL/M 50% — for extruded samples. Calorimetric measurements in the mode of the temperature-modulated heat flow of the sample were performed by using a differential scanning calorimeter DSC25 produced by TA Instruments (USA) in a standard aluminum crucible in the pure N_2 atmosphere at the flowrate of 70 ml/min. The samples were heated in the temperature range of -10 to 150°C with the rate of 10°C/min. The heat flow was modulated sinusoidally with the 60 s period and ±1°C amplitude. To remove the sample thermal history, it was heated from 20°C to 150°C with the rate of 20°C/min. The ΔH_m enthalpy variation was calculated via the melting peak area using special program code „TRIOS“.

To get an X-ray pattern of the PCL–Monament-101 composite granules, the granules were pressed in plates and then fixed in a cuvette. The X-ray patterns were detected in the angle range of $2\theta = 4{-}60^\circ$ at the Crystal Physics Laboratory using the facilities of the RAS SO KSC FRC Common Use Center, namely, powder X-ray diffractometer D8 ADVANCE (Bruker AXS, West Germany). The radiation wavelength corresponded to the conventional CuK_α line. The acquired data was processed using program code Eva 5.2.0.3 comprised in the diffractometer software. Based on the X-ray diagrams of the samples, their crystallinity was estimated via formula $C_x = 1 - S_1/S_2$, where S_1 is the area confined by the curve of the amorphous background (amorphous halo), S_2 is the total area under the X-ray curve. The areas were calculated by integration with subtracting the instrumental background. Taking into account that parameter S_2 comprises, among others, the area under the montmorillonite peaks, parameter C_x to be determined is the total crystallinity of the composite sample which is a superposition of the polymer matrix and montmorillonite crystalline phases.

Polycaprolactone is a thermoplastic polymer consisting of the amorphous phase by 50.3–48% and of the crystalline phase by 49.7–52%. Thermal impacts, mechanical loads and inclusion of fillers promote variations in the polymer crystallinity, which is connected with arising of extra crystallization nuclei, lamella thickening, or a certain arrangement of the filler in the polymer. The polymer crystallization in the presence of fillers are affected mainly by two factors: surface filler–polymer interaction creating stressed regions on the phase interface, and the presence in the polymer medium of the filler affecting the system viscosity, which is expected to prevent the crystallization. In this work, an increase in crystallinity relative to that in pure PCL (see the table) is observed in almost all granules, which is not fully typical of such systems. This phenomenon is associated with the fact that sufficiently crystalline montmorillonite existing in the polymer matrix plays the role of a crystal-nucleating agent. Otherwise, the polymer portion that has passed to the near-surface boundary layer could not participate in the crystallization, and the polymer would become less crystalline. Crystallinity in the granules obtained from melt increased with increasing clay content in the polymer matrix and reached 61% at the maximal inclusion of filler „Monament-101“. In the granules obtained from solution, no correlation between the crystallinity degree and clay content was observed. The heterogeneous effect of the „Monament-101“filler is connected with the composite fabrication procedure itself, namely, with the rate of solvent evaporation and isothermal crystallization. Crystallinity in the sample of granules filled with montmorillonite by 10% decreased and became 48%, which was probably caused by loosening of the supramolecular structure and formation of defective regions which hindered the PCL crystallization and decreased the crystallinity.

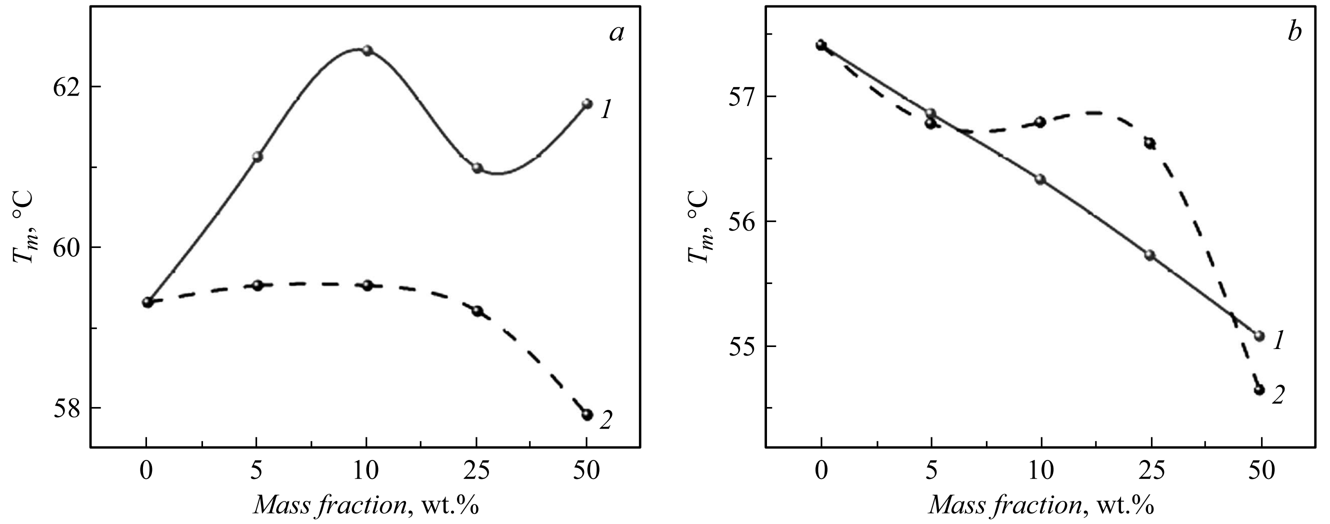
Properties of the PCL–and–„Monament-101“based granules obtained by different methods (the second heating data)

Sample	T_m, °C	ΔH_m^*, J/g	C_x, %
PCL	57	64.4	52
Granules from solution			
S_PCL/M 5%	56.8	38.2	58
S_PCL/M 10%	56.3	46.3	48
S_PCL/M 25%	55.8	25.3	53
S_PCL/M 50%	55.1	35.7	67
Granules from melt			
E_PCL/M 5%	56.8	64.6	54
E_PCL/M 10%	56.7	62.7	56
E_PCL/M 25%	56.6	53.3	56
E_PCL/M 50%	54.6	36.4	61

*ΔH_m is the enthalpy variation $\Delta H = \Delta U + \Delta(pV)$.

DSC data on the primary heating of the composite granules obtained by the solution-based techniques exhibits a temperature increase from 59 to 62°C that was not characteristic of granules obtained by extrusion where a gradual decrease in the melting point was observed (T_m) to 57.7°C (see the figure, a). Such a temperature increase is connected with evaporation of moisture and volatiles.

The second heating results lead to the conclusion that introduction of the filler insignificantly affects T_m of the granules (see the table). As the filler content increased to 50%, the granule T_m decreased by 2°C. Granules obtained from solution exhibited linear variation of the melting point (see the figure, b). Filler „Monament-101“ in composite granules confines spatially the PCL crystal growth thus promoting the formation of rather small and defective crystals. Some of the crystallization nuclei are on the surface of the second component. This is the so-called epitaxial crystallization. This crystallization mechanism provides the formation of small defective crystals on the substrate. On reaching the critical thickness, crystals typical of this substance begin forming. Small-size crystals are characterized by lower melting points than large-size ones, which can explain the temperature decrease with increasing crystallinity. The melting enthalpy of the obtained composite granules decreased by 1.25–2.5



DSC data for granules based on PCL and „Monament-101“filler obtained by different methods: from solution (*1*) and from melt (*2*). *a* — the first heating, *b* — the second heating.

times with respect to that of pure PCL, which is a result of the closed-packed arrangement of macromolecules whose intermolecular interaction energy exceeds the pre-crystallization value. Thus we may conclude that filler „Monament-101“ is able to act as a nucleating agent and promotes the increase in the composites crystallinity. Both the methods affect the granule characteristics, however, behavior of the granules obtained with adding montmorillonite to the melt for extrusion is better predictable than that in case the „from-solution“ technique is used.

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Conflict of interests

The authors declare that they have no conflict of interests.

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