Оглавление

Введение

Additive manufacturing (AM) alias 3D printing translates computer-aided design (CAD) virtual 3D models into physical objects. By digital slicing of CAD, 3D scan, or tomography data, AM builds objects layer by layer without the need for molds or machining. AM enables decentralized fabrication of customized objects on demand by exploiting digital information storage and retrieval via the Internet. The ongoing transition from rapid prototyping to rapid manufacturing prompts new challenges for mechanical engineers and materials scientists alike. Because polymers are by far the most utilized class of materials for AM,
The range of polymers used in AM encompasses thermoplastics, thermosets, elastomers, hydrogels, functional polymers, polymer blends, composites, and biological systems. Aspects of polymer design, additives, and processing parameters as they relate to enhancing build speed and improving accuracy, functionality, surface finish, stability, mechanical properties, and porosity are addressed. Selected applications demonstrate how polymer-based AM is being exploited in lightweight engineering, architecture, food processing, optics, energy technology, dentistry, drug delivery, and personalized medicine. Unparalleled by metals and ceramics, polymer-based AM plays a key role in the emerging AM of advanced multifunctional and multimaterial systems including living biological systems as well as life-like synthetic systems. [9]

Нужны метариалы [5]

Такие материалы делает, например, Ultem [ССЫЛКА] Ввиду сами-знаете-чего, актуальна разработка и изучение отечественных аналогов. В ИВС РАН синтезированы термопластичные частично кристаллические ПИ гомологического ряда Р-ОДФО на основе отечественного резорцино-вого диангидрида Р (1,3-бис-(3,3,4,4-дикарбоксифенокси)-бензол) и че-тырехядерного диамина ОДФО (4,4-бис(4-аминофенокси)бифенил) мето-дом химической (с использованием катализаторов) и термической ими-дизации [Юдин В. Е., Светличный В. М. // Высоко-молекулярные со-единения, серия С, 2016. Т. 58. №1. С. 19]. Исследованы форма, размер частиц (фракци-онный состав ПИ порошка) [13] СЛС - кратко [ССЫЛ-КА]

Применяется для индустрии (3д review)

Таким образом, многообещающим направлением в СЛС является использование high-performance термостабильных термопластичых полимеров и модификация полимеров with small additives наночастиц. Главные преимущества СЛС перед другими технологиями, это [vaganov corrected]: :

- свойства изделий, полученных методом СЛС схожи со свойствами изделий полученных традиционными методами, такими как extrusion, injection molding, hot pressing, etc.

- теоретически, в технологи СЛС может быть использова любой материал, который можно получить в порошке и расплавить при increasing temperature

- при печати сложых продуктов не нужно дополнительных опорных элементов.

Researches on the application of other polymers in SLS technology are very limited. In addition to polyamide, polystyrene and polycarbonate are used as a starting material for SLS.12,13 [vaganov corrected]

"Анализ современной литературы показывает, что на сегодняшний день исследования в области применения термостойких полимеров для СЛС сосредоточе-ны лишь на семействе полиэфиркетонов [Berretta S., Ghita O., Evans K. E. // European Polymer Journal, 2014. Vol. 59. P. 218–229]. На данный момент практически отсутствуют сведения об использовании других клас-сов термостойких полимеров, таких, например, как полиимиды (ПИ). Кроме того, существует ряд проти-воречивых сведений о влиянии тех или иных параметров на процесс СЛС и конечные свойства материала в целом. В связи с этим, с научной и технической точки зрения весьма перспективным представляется иссле-дование закономерностей формирования структуры при СЛС порошков ПИ, изучение процесса их сплав-ления в зависимости от свойств порошка, содержания нанонаполнителей, а также параметров СЛС. [13]

Объект исследования... Соответственно, **предмет** исследоания – морфология и кристаллическая структура.

Глава 1

Теория

1.1 Селективное лазерное спекание

1.1.1 Технология

Polymer laser sintering (LS) is an important additive manufacturing (AM) technology. Individual and complex parts are directly produced from CAD data without the need of specific tools. The raw material is a polymer powder, which is deposited layerwise and melted selectively with a laser. Built parts are embedded in residual unmolten powder
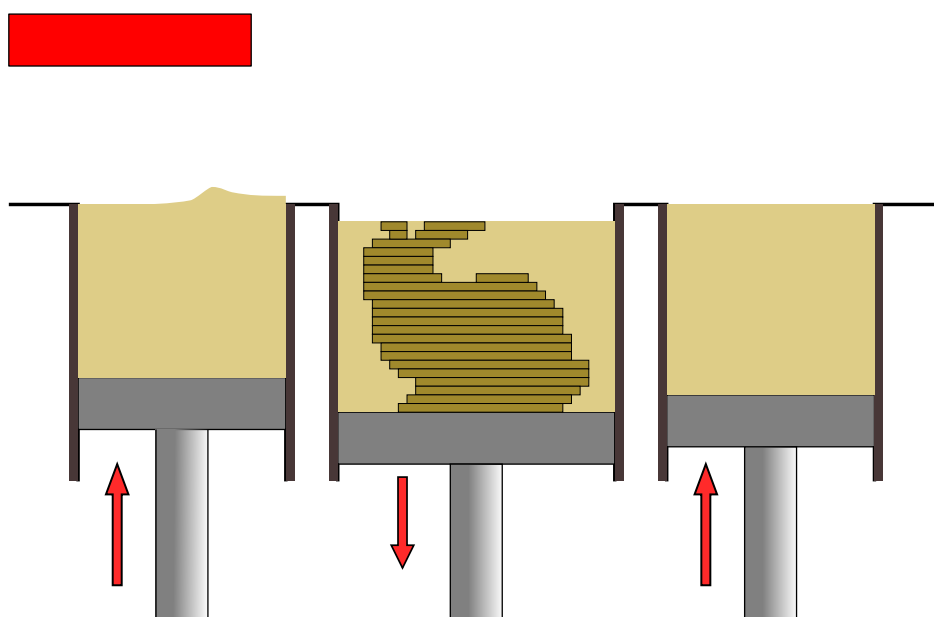

Рис. 1.1: [WIP]Принцип работы SLS-принтера

Что это вообще

Общий принцип. Процесс печати изделия изображен схематически на рис. 1.1. The feed powder hopper (1) dispenses a polymer powder into a recoater unit (2) which moves in x direction and thereby recoats thin powder layers onto the build platform (5). Residual powder is collected in an overflow bin (6). After each layer, the platform moves down in z direction. Typical layer thicknesses are about 50 to 200 mm. During the build process, the so-called part cake (3) "grows" from the bottom to the top. By volume, it typically consists of about 90of about 10surface is preheated with infrared heaters (7) up to 2 to 5 K below melting temperature of the material. The energy needed to fully melt the powder is brought in with a CO2 laser (8) that selectively melts the desired slice geometry. In this phase, unmolten powder and molten parts remain quasi-isothermal within the same layer.7 This so-called temperature window has to be lower than the melting temperature and higher than the recrystallization temperature of the material8 in order to prevent warpage during the manufacturing process. Hence, heating up the whole part cake is a prerequisite for a reliable LS process. To reduce oxidation, the process chamber is purged with nitrogen (residual oxygen <2the part cake is first cooled down within the machine for about 10 h (nitrogen flow) and then outside of the machine until the core temperature is below glass transition temperature. Then, the parts are removed from the, unmolten powder. With total build heights of up to 600 mm, typical layer thicknesses of about 100 mm and layer times of about 10 of 40 s, the overall manufacturing process may take many hours or even days,4 resulting in various powder ageing effects.

Polymer laser sintering (LS) is an important additive manufacturing (AM) technology. Individual and complex parts are directly produced from CAD data without the need of specific tools. The raw material is a polymer powder, which is deposited layerwise and melted selectively with a laser. Built parts are embedded in residual unmolten powder

Особенности сравнению с традиционными методами. Thereby, product development times can be reduced tremendously. Other advantages are, for example, the fast and costefficient production of low-volume, individual and complex parts and structures.3

Особенности по сравнению с другой 3д-печатью.

1.1.2 Сращивание частиц порошка при СЛС

Laser-based consolidation of 3D parts from layers of powder material pre-deposited on a 'build platform' is commonly referred to as Selective Laser Sintering (SLS) or Selective Laser Melting (SLM). The distinction between SLS and SLM is rough, vague and does not cover all

Классификация схематически показана на рис.1.2
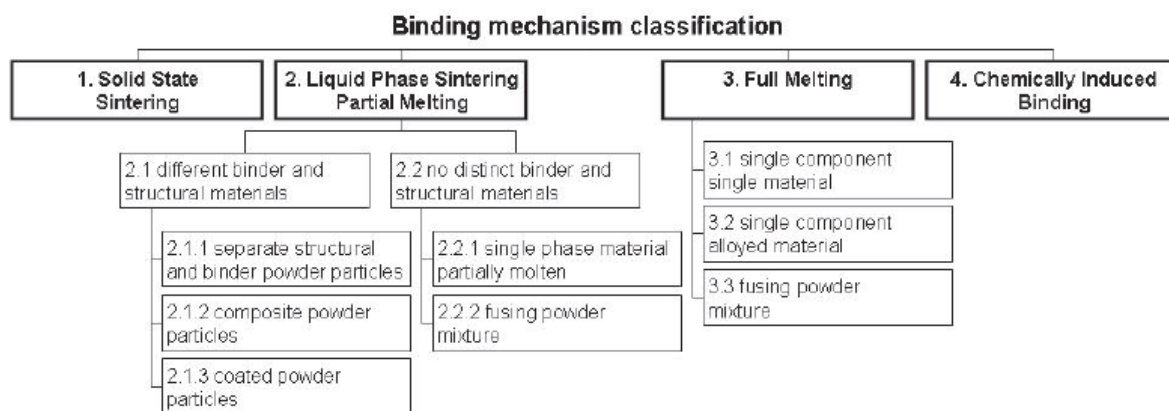
Рис. 1.2: Механизмы консолидации порошка

Симуляция процесса close-up. Высокая интенсивнсть лазерного излучения позволяет быстро нагревать небольшие участки материала, создавая большие градиенты температур [6].
Симуляция СЛС показывает, что у композитных порошков будет сильно отличное распределение температур, особенно глубина плавления. (по крайне мере в полиамидах)[6]. Экспериментальное исследование становится эфеективнее, если есть модель процесса. Какие нужны параметры для модели?

1.2 Требования к материалам для СЛС

The availability of suitable LS polymer powders is quite limited. The manufacturing process requires certain polymer properties, mainly a large process window and a low melt viscosity,4 and particle/powder properties, for example, a good flowability and high bulk density.9,10 Due to these limitations, the majority of all LS applications is currently based on polyamide 12 (see Figure 2)

Конечные характеристики изделия, полученного по технологии СЛС, во многом зависят от от свойств начального порошка (морфология, размер, распределние размеров, объемная плотность, термические свойства,

вязкость, поверхностное натяжение) и параметров спекания (мощность лазера, скорость сканирования, диаметр пятна излучения лазера).

1.2.1 Механические характеристики

первая глава из [2]

1.2.2 Тепловые характеристики

Built parts are embedded in residual unmolten powder, the so-called part cake, which undergoes thermal ageing effects due to the exposure to high temperatures for long times during the manufacturing process. Hence, the recyclability of the unmolten powder is limited. [8]

1.2.3 Морфология частиц порошка

Морфология частиц определяет пространственное расположение частиц порошка (stacking degree) относительно друг друга. Сферические (с гладкой поверхностью) частицы имеют высокую плотность упаковки. Они обеспечивают сыпучесть in systems of applying the material with minimal resistance. В добавок, сферические частицы хорошо связываются в процессе спекания.Показано, что during the transition from powder particles with predominantly spherical morphology to particles of irregular shape of the same material, the elastic modulus decreases by almost 40 %. (найти ссылку ,потом перевести). Таким образом, сферический частицы с хорошей сыпучестью и высокой плотностью упаковки представляют идеальные характеристики стартового пороша для использщования в СЛС. В то же время использование частиц неправильной формы с большой вариацией в размерах ведет к созданию продуктов с более высокими механическими характеристиками в сравнении с использованием mainle сферических частиц с узким распределением размеров.

1.2.4 Кристалличность

1.2.5 Прочее

1.2.6 Полиэфиримиды ряда R-BAPB

Что это
Особенности
Намеренные ранее характеристики
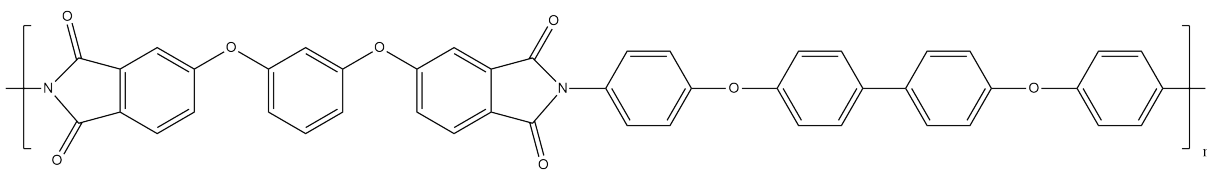Использование в промышленности
Композиты

Рис. 1.3: Структура полимера Р-ОДФО [3]

Короче, они збс и подходят для СЛС
Что нужно выяснить.

1.3 Кристаллическая структура полимеров

Что ее характеризует Поскольку кристаллические области в этих полимерах формируются из длинных цепей, их кристаллизация сложна и сильно чувствительна к маленьким изменениям в полимерной (compostion), добавкам, температуре и механическим воздействиям.
Не все полимеры кристаллизуются, а те, что кристаллизуются, редко делают это полностью: только небольшая часть crystallizable цепей incorporated into crystalline domains, а остальные segregate into amorphous domains. Степеь кристалличности и характеристики кристаллических domains являются самыми важными морфологическими характеристиками, которые определяют физические свойства такие как плотность, mechanical strength, processability, permeability and degradability частичнокристаллического полимера.
Степень кристалличности типичного полимера варьируется в пределах от 10 до 80 %. Сравните с металлами, которые, за исключением металлических стекол, почти всегда полностью кристалличны, и ceramics, которые или полностью кристалличны, или аморфны.
[12] или [11]

Кристаллическая структура полимеров менее идеальна чем кристаллы соединений с меньшей молекулярной массой. Как правило полимерные материалы находятся в метастабильном состоянии, то есть являются частично кристаллическими и частично аморфными. Большинсво полимеров частичнокристалличны по структуре, кристаллические структуры часто формируются при охлаждении расплава, что контролирует механические и физические свойства частичнокристаллических полимеров. Ввиду высокой вязкости полимерных расплавов, полимеры кристаллизуются очень медленно при температурах ниже температуры плавления (T_m), даже при высоком переохлаждении (high supercooling)
Кристаллическая структура и степень кристалличости зависят от молекулярной структуры полимера, условий (growth conditions), присут-

ствия инородых частиц в решетке, температуры кристаллизации, скорости охлаждения и т.д.

Они могут быть оценены из рентгеновской дифракции, измерений плотности, термического аналища и т.д.

1.3.1 Кристаллиты

Морфологии полимерных кристаллов можно условно поделить на ламеллярные и фибриллярные кристаллы. В процессе ламеллярной кристаллизации, направление роста перпендикулярно направлению цепи, возникает складываение цепочки.Во время фибриллярной кристаллизации, наплавление роста кристалла совпадает с направление цепи, и в решетке кристалла возникают highly extended chain conformations. Такие материалы имеют высокие механические свойства. Кристаллизация существенно меняет физические и механические свойства полимерных систем.

Studying the crystallization behavior, though complicated, is necessary mainly in relation to the physical and mechanical properties of polymers. If crystallization would be absent in polymer systems, then the whole mechanical performance of polymers depends on the glass transition temperature (Tg). If glass transition is the only determining factor for the properties of the polymers, then polymers such as polypropylene (PP) and PE would have been rubbers at ambient temperature. However, in these polymers, due to crystallization, the stiffness is retained at acceptable and controllable values up to the melting temperature (Tm).

Multiphase polymer systems commonly consist of polymer blends, composites, nanocomposites, interpenetrating polymer networks, block copolymers, and polymer gels. Crystallization in multicomponent polymer-based systems represents the main physical characteristic that allows for control of the material properties.

The presence of nanoparticles can also limit themotion ofmolecular chains, resulting in suppression of the crystalline perfection and crystallinity of polymer crystals.

Crystallization is a first-order transition and a thermal process in polymers. The polymer chains are aligned and folded together to form an ordered chain region, which is called lamellae. The lamellae are composed of spherical aggregates called spherulites. The crystallization process changes the density, symmetry, and phase transition and thus controls the properties of the end products. Crystallization commonly proceeds by nucleation of a fiberlike structure followed by lamellar structure formation. The spherulites grow away from a nucleation site.

Nowadays polymer composites are commonly used in aerospace, sport goods, automobiles, industrial equipment, etc. Polymer composites are polymer-based matrix with some form of materials embedded in the matrix, as reinforcements.

Polymer composites are classified on the basis of the size of filler particles into microcomposites and nanocomposites.

(Это в планы на будущее) Many experimental techniques can be used to study the crystallization kinetics of nanocomposites. The most common techniques used to study the crystallization kinetics in the nanocomposites are DSC, optical microscopy, and WAXD.

The crystallization kinetics of polymer composites and nanocomposites gained great interest due to the fact that fillers act as an effective nucleating agent in the polymer matrix. With the advancement of nanotechnology, the focus is now shifting toward understanding the crystallization properties of materials in nanodimensions and thereby tune the properties for diversified tailored application.
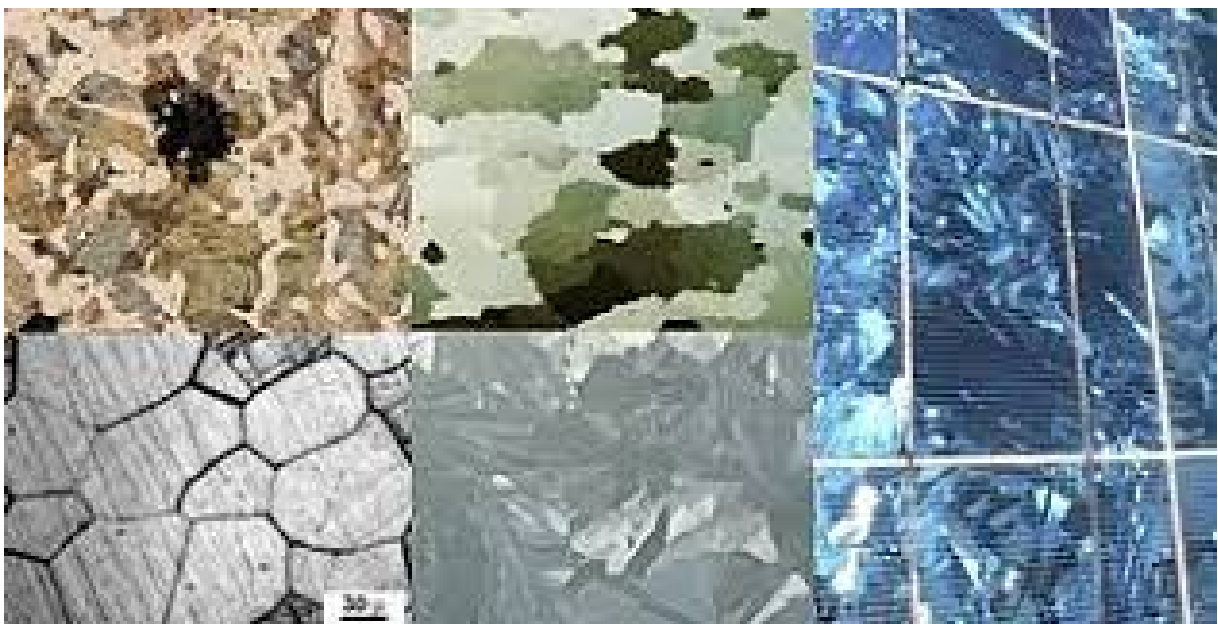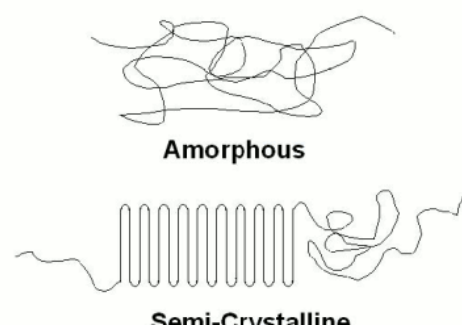
Это все из [11]

Рис. 1.5: Типы кристаллитов

1.3.2 Частичная кристалличность

Properties of the semicrystalline polymers can be understood, for the most part, using a simple two-phase model that assumes that

Amorphous

Semi-Crystalline

the two phases, the crystalline and the amorphous, can be easily distinguished. If an intensive property ϕ (e.g., specific volume, specific heat) of the crystalline and amorphous phases, ϕ c and ϕa, respectively, can be measured, and if we assume that contributions of the two phases are additive, then

$$\phi = \phi_c x + \phi_a(1 - x)$$

where x is the fraction of the crystalline phase, which ideally is the mass fraction (x_m) but depends somewhat on the technique (это из [12]) The smallest organized units of polymer chains are crystallites or lamellae. These further assemble to form fibrils and spherulites. The occurrence of spherulites and fibrils can be used to identify if the polymer is crystalline or not, and to measure local crystallinity

Units such as lamellae and fibrils (nanometers) can be visualized only by transmission electron microscopy, whereas larger units such as spherulites (micrometers) can be monitored by optical microscopy. Crystalline features can also be imaged using contact mode atomic force microscopy, for instance, by correlating the surface roughness and local stiffness to crystallinity. Studies of the crystalline growth, formation of fibrils, and growth of spherulites lead to a better understanding of the crystallization behavior of polymers.

The two-phase model implied in Eq. (3.1) is only an approximation because there can be a continuum of structures from large, defect-free single crystals to the truly amorphous domains with liquid-like order. Because of the restrictions imposed by long polymer chains, defects are invariably present in the crystal lattice, and the polymer crystallites are small and disordered. Conversely, the amorphous domains possess some degree of positional
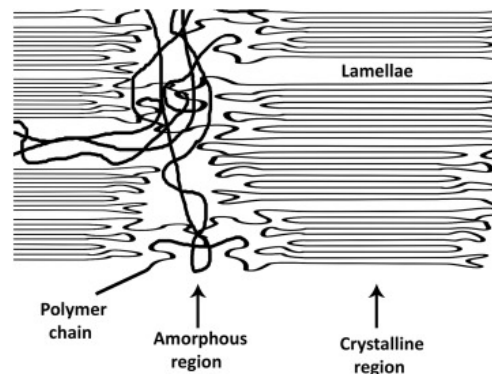
Рис. 1.6: К определению кристал-личности полимеров

and orientational correlations, and there is experimental evidence for both rigid or ordered and soft or fluid amorphous phases

it may not always be possible to distinguish between the signatures of the crystalline and amorphous phases. Nevertheless, a two-phase model with an approximate crystalline phase and an amorphous phase, and sometimes an

additional ordered phase, mostly due to oriented amorphous domains, is often used.

1.3.3 Влияние на макроскопические параметры

Глава 2

Эксперимент

2.1 Исследование кристаллической структуры

Тырим описание методов и формулы из [12] Кристалличность полимеров может быть проанализирована, если обнаружить раличия в характеристиках аморфных и кристаллических областей. Приведем широко используемые методы, с помощью которых определяется кристалличность.

2.1.1 Плотность

The most basic is the small differences in the density of the crystalline and amorphous regions that makes it possible to use density measurement for the evaluation of the polymer crystallinity. При аддитивности по объему:

$$\%_{x_m} = \frac{\nu - \nu_a}{\nu_c - \nu_a} \cdot 100 = \frac{\rho_c}{\rho} \cdot \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

При аддитивности по массе:

$$\%_{x_\nu} = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

Точность измерения < 0.1 кг/м3
The density of the crystalline phase can be calculated from the crystallographic unit cell parameters. The density of the amorphous phase can be obtained by extrapolating to room temperature the specific volume of the melt measured at various temperatures by dilatometric methods [16,17]. The crystalline and the amorphous densities can also be determined experimentally by extrapolating the densities of a series of samples with known crystallinities as measured by XRD.
Короче нужен будет рса

14

2.1.2   Термический анализ

Equally fundamental is the thermal characteristics of the crystalline and the amorphous regions. Because crystalline domains melt upon heating, and amorphous domains do not, heat of fusion can be a used as a measure of the degree of crystallinity.

The amount of energy absorbed depends on the degree of crystallinity. This energy can be determined using

differential scanning calorimetry (DSC). DSC measures the amount of heat absorbed or released by the sample relative to a reference (an empty pan) as it is taken through various thermal transitions at a constant heating or cooling rate, and under isothermal conditions as a function of time.

The mass percent crystallinity (xm) of a specimen can be calculated from the measured heat of fusion (DHm) and the knowledge of the value for 100% crystalline material ΔH_m^0 from the relation

$$\%x_m = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \cdot 100$$

The term DHc is the heat of cold crystallization. A typical DSC scan consists of a heat cool reheat cycle, all three being done at a rate of 10 C/min. Because materials change during heating as well as upon cooling, the crystallinity should be determined from the scan obtained during the first heat.

The implementation of Eq. (3.5) into practice to evaluate the crystallinity is not straightforward!!!

issues. First, a proper baseline has to be drawn for precise determination of the crystallinity.

Second, crystallization of the sample during heating, cold crystallization, is a serious problem in evaluating the crystallinities of samples with low levels of crystalline order.

2.1.3   Спектроскопия

At the structural level, the conformation of the chains is different in the crystalline and the amorphous regions. Thus spectroscopic methods such as infrared (IR) and Raman spectroscopy can be used to follow crystallization if the absorption bands of the chains' crystalline and amorphous conformations can be easily identified. Because the mobilities of the chains in the amorphous and the crystalline regions are different, solid-state nuclear magnetic resonance (NMR) can be used to characterize polymer crystallinity.

IR spectroscopy, Raman spectroscopy, and NMR are the three common

spectroscopic methods used to analyze the structural characteristics, such as conformation, stereoregularity, orientation, and inter- and intramolecular interactions of polymers [38]. These techniques are also used for crystallinity determination after calibrating with other techniques such as density or XRD.

IR absorption or reflection spectra from crystalline regions contain additional peaks that are absent in amorphous regions with the same composition. These signals may originate from deformation vibrations of the regular arrangement of molecular chains [38]. A degree of crystallinity can be estimated by comparing the intensity of these bands [39].

The two vibrational spectroscopic techniques, IR and Raman spectroscopy, rely on the differences in the conformation and the packing of the chains in the crystalline and amorphous regions. NMR methods rely on the differences in either the electronic environment or the mobility of the nuclei on the chains in the two regions.

2.1.4 MAPPING OF CRYSTALLINITY

The discussion thus far assumes that the crystallites that constitute the crystallinity are uniformly distributed throughout the sample. This is not always the case. Temperature and stress gradients that are present during processes such as extrusion and injection molding give rise to crystallinity gradients from surface to the bulk [50,51]. Such skinecore structures can be mapped by scanning IR or Raman techniques with a spatial resolution of w100 mm.

The figure shows that the skin is predominantly amorphous or in the g crystalline form, whereas the core is more crystalline and is in the a crystalline form. Such crystallinity gradients occur because the polymer cools rapidly at the surface, thus quenching the polymer melt at the surface into its amorphous phase, and at the same making it to crystallize in the rapidly crystallizable g form. In contrast, in the core of the bar, where the polymer cools more slowly, the polymer crystallizes in the thermodynamically more stable a form. Such variations in the structure can also be mapped using scanning microbeam X-ray diffraction (m-XRD) techniques and by grazing incidence diffraction (GID)

m-XRD techniques can routinely sample areas 50e100 mm in diameter. It has been used to map skinecore structural gradients that occur in a Kevlar fiber with a 3-mm beam

In GID, X-rays are incident at a very small angle so that diffracted X-rays correspond to the crystallinity within top surface layers. A depth profile of

the crystallinity can be generated by analyzing a sequence of scans obtained at a series of incidence angles

Such mapping of the crystallinity gradients is important in understanding the effect of process variables such as temperature and cooling rates on the performance of the fabricated devices.

Короче, раньше никто карты такие особо не строил, а если и строил, то не публиковал.

2.1.5 Дифракция

Finally, polymer chains are packed into crystal lattices, and these lattices, even if they are disordered, give rise to crystalline diffraction peaks in wide-angle X-ray scattering (WAXS) patterns. Thus the intensity of the crystalline peaks in X-ray diffraction (XRD) can be used as a direct measure of the polymer crystallinity. In addition, when a polymer crystallizes, it often forms large-scale structures such as lamellae and fibrils. These larger structures can be observed using small-angle X-ray scattering (SAXS) and electron microscopy

The two commonly used X-ray scattering techniques to examine the crystalline features of semicrystalline polymers are: WAXS, also called wide-angle X-ray diffraction (WAXD), and SAXS. WAXS is sensitive to atomic and molecular structures and thus provides a direct measure of the crystallinity. SAXS is sensitive to mesoscale structures and reports on the effect of changes in the crystallinity on the morphology of the polymer.

2.1.6 Микроскопия

The even larger structures such as spherulites formed by the assembly of lamellae and fibrils can be studied by optical microscopy. These techniques will be discussed in this chapter.

2.1.7 Сравнение и обоснование

табличка Crystallinity in semicrystalline polymer is a valuable concept. However, it represents different entities in different techniques. Density is a measure of the macroscopic volume, and differences in the density brought about by differences in the packing of the chains in the amorphous and crystalline regions are used to determine the crystallinity. IR and Raman spectroscopy depend on the local conformational differences of the chains in the amorphous and crystalline regions. NMR senses the difference in mobility in the amorphous and crystalline segments and sometimes the

rigid amorphous segments, the structure of the interfacial regions between crystalline and amorphous regions, and the diffusion across these interfaces. DSC relies on the melting transitions exhibited only by crystalline domains. X-ray scattering reveals the state of the internal order and the size of the crystalline regions and SAXS about lamellar structures. Optical microscopy provides information about spherulitic morphology. Because different aspects of the crystallinity are being measured by different techniques, the value determined by the various techniques is referred to as a CI (e.g., Eq. 3.10) that is specific to a technique (CI by density, CI by XRD, etc.) rather than as the degree of crystallinity

Crystallinity should be measured by XRD whenever possible because the domains are regarded as crystalline or amorphous depending on their diffraction pattern. Other methods, especially spectroscopic techniques, are often calibrated using XRD values to convert the technique-dependent crystallinity to the mass fraction of crystallinity. Because even small crystallites, too small to be seen as crystalline by XRD, can show melting transitions, DSC crystallinities can be higher than the XRD crystallinities. XRD measures the crystallinity as reflected by the long-range ordering of the polymer chains. Spectroscopic techniques, IR and Raman spectroscopy, measure the crystallinity as reflected in the short-range interactions, which may or may not correspond to crystallinity as defined by long-range order. Because the signatures of the crystalline and the amorphous regions in various techniques may be affected to different extents by imperfections, interfacial interactions, and other effects, there can be disagreement in the crystallinity values obtained by different methods. Although spectroscopic techniques are secondary techniques, they are fast and more readily available than XRD and density. Hence they are preferred for online measurements, and in instances where other techniques cannot be used. Density measurements give only crystallinity values, whereas other techniques described here measure more than just the crystallinity of the polymer. They are useful in understanding the subtle but important characteristics of the crystalline component of the polymer. This is especially true for techniques such as NMR, IR, and microscopy. Even if these techniques are not used to measure the degree of crystallinity directly, they can be extremely useful to explore other aspects of crystalline domains.

2.2 Исследование структуры с помощью дифракции рентгеновского рассеяния

2.2.1 Синхротронное излучение

когерентные источники, йоу!

2.2.2 Упругое рассеяние

2.2.3 2D-снимки, порошковая дифракция

2.2.4 Неупругое рассеяние,гало

эффекты от аморфной части

2.2.5 WAXS

XRD, is the most fundamental of all the methods for determining the crystallinity against which the results from other methods may be compared. This is because the basic concept of crystalline order arises from the ordered packing of the polymer chains that give rise to sharp diffraction peaks. In contrast, the disordered chains, with liquid-like disorder, give rise to a broad amorphous halo. The atomic planes that make up the crystalline structure give rise to diffraction peaks at certain scattering angles, 2q, corresponding to the d-spacings as given by Bragg's law:

$$\lambda = 2d \sin\Theta$$

The position of the diffraction peaks are sometimes indicated by the scattering vector q, where $q = 2\pi/d = 4\pi \sin\Theta/\lambda$. The ratio of the area under the crystalline peaks to the total scattered intensity is used to calculate the crystallinity.
Assuming that the scattering can be separated into amorphous and crystalline peaks (two-phase model), the mass fraction of crystallinity xm can be calculated as the ratio of the integral of the diffraction intensity scattered by the crystalline fraction to the total coherent scattered intensity

$$X_m = \frac{\int_0^\infty q^2 I_c(q) dq}{\int_0^\infty q^2 [I(q) - I_{Compton}(q)] dq}$$

where Ic(q) is the intensity in the crystalline peaks, I(q) is the total scattered intensity, and ICompton(q) is the intensity due to Compton scattering.

19

Routine analysis is carried out using a diffraction scan over a smaller q range of 0.5-3 A.

Such scans are profile fitted to crystalline peaks and amorphous halos as shown in the figure, the areas Aa and Ac of the amorphous and the crystalline peaks, respectively, are determined, and a crystalline index (CI) is calculated using the relation

$$CI = \frac{A_c}{A_a + A_c} \cdot 100$$

As can be seen from the figure, the contribution of the crystalline disorder over this angular range is minimal, and hence Eq. (3.10) yields a reasonably accurate value for the crystallinity.

The degree of crystallinity in polymers is a measure of the degree of order in the form of a fraction of the ordered molecules that are able to diffract X-rays. But identifying and resolving the observed scan into crystalline and amorphous peaks can be far from trivial when the crystalline regions are highly disordered

The peaks that are sharp enough to have arisen from domains >30 A in size are generally regarded as crystalline peaks. For instance, a peak at 2q = 24 degrees , typical for interchain scattering, with a full width at half maximum of at least w2.5 degrees (at 2q w 20 degrees) corresponding to about three to five unit cells, is considered crystalline. Domains smaller than 30 A are considered amorphous.An equally important factor is the determination of the proper baseline for background subtraction, and use of an appropriate profile for the amorphous halo (Wile 2016) XRD scans are used in the calculation of the crystallite size and the disorder within the crystals.

The method described thus far applies to unoriented samples.

2.2.6   SAXS

SAXS patterns from polymers, both amorphous and semicrystalline, invariably consist of a central diffuse scattering at low q values (<0.05 A) due to voids and fibrils. Semicrystalline polymers often show additional discrete reflections at slightly higher q values. These reflections arise from the organization of polymer crystals and amorphous domains, each 5e50 nm in size, into larger length scale structures consisting of lamellae and fibrils.The positions of these discrete reflections are used to calculate a long spacing or long period using Bragg's law and they correspond to the spacing between these large crystalline features. The discrete reflections that occur along the equator (perpendicular to the chain axis) are due to the separation of the fibrils. These fibrils could be from lamellar stacks [e.g., nylons and polyethylene, poly(ethylene terephthalate), polypropylene] or from fringed

micelles (e.g., cellulose and some liquid crystalline fibers). A second class of discrete reflections that occur along or close to the meridian (chain axis) arise from lamellar stacks within which the folded chain crystalline lamellae 5e25 nm in height are separated by 1e3 nm thick noncrystallizable amorphous chain segments between the lamellae.

evaluation of the fraction of the crystalline lamellae, and hence the crystalline content, by resolving the observed scan into central diffuse scattering (Id) and the lamellar peak (IL), after subtracting a suitably chosen background (Ib).

A linear crystallinity can be calculated from these lamellar reflections as the ratio of lc/L, where lc is the height of the crystals and L is the lamellar spacing. A more complete analysis is usually carried out with unoriented polymers using a 1D scan through the lamellar peak (Fig. 3.3C). The analysis takes into account the differences in the electron densities of the crystalline and amorphous regions [36]. The electron density of the crystalline regions is greater than that of the amorphous regions. This electron density difference (Dr) causes X-ray to be scattered at small angles. From a SAXS pattern, a quantity called the invariant (Q) can be calculated from the observed intensity, I(q), and is related to the volume fractions of the crystalline (fc) and amorphous (fa) components.

$$Q = \int_0^\infty I(q)q^2dq$$
$$Q = 2\pi^2\Delta\rho^2\varphi_c\varphi_a$$

I(q) needs to be expressed in terms of electron units, and the scattering due to local fluctuations and other artifacts needs to properly subtracted. Integrations are typically carried out from q = 0.01 to 1 A-1

2.3 Материалы

Для исследования структуры взяты образцы порошка Р-ОДФО и пленки, полученные на лазерной установке методом СЛС (рис. 2.1). Характеристики частиц: размер 444 для синтезна с 20% ПЛА и 555 для другого синтеза. Дисперсность(?) частиц, таким образом, конкролируется условиями синтеза (?).
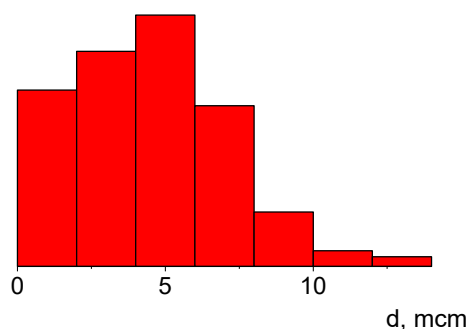
2.4 Оборудование

Измерения проводились на микрофокусной линии D13 Европейского центра синхротронного излучения (ERSF). Фото и схема ускоряющего
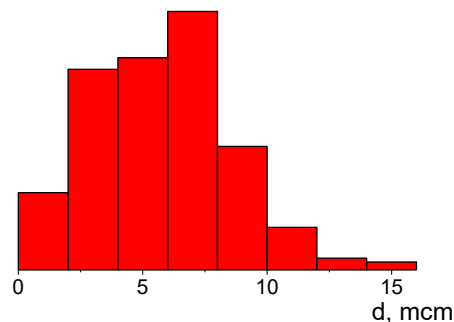
Рис. 2.1: Caption

кольца показаны на рис. 2.2.

Рис. 2.2: Синхротрон ERSF

А работает это так: (тут еще картинка со схемой). Тогда получается большая интенсивность, бриллианс, статистика.

2.4.1 Детектор

2.4.2 Размещение образца

2.5 Схема эксперимента
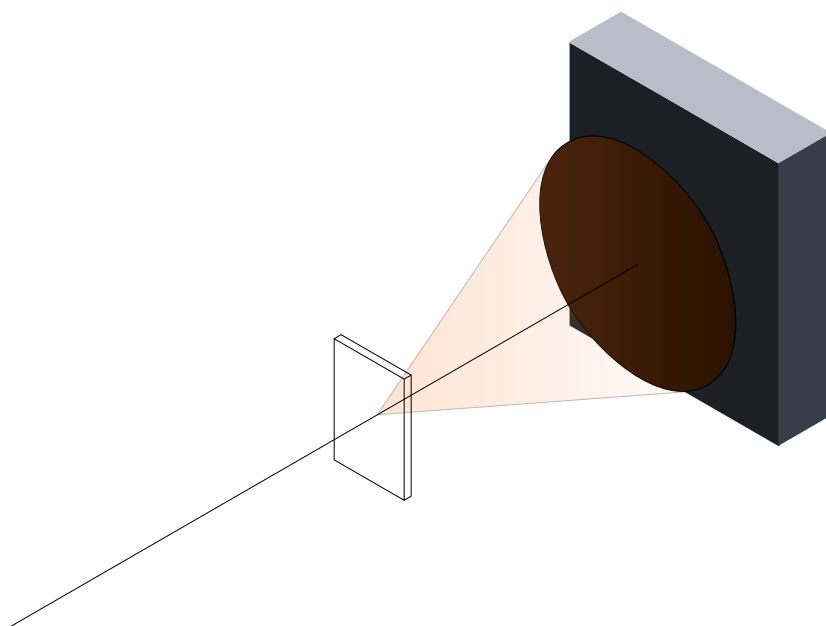
Принципиальная схема изображена на рис. 2.3.

Рис. 2.3: [НЕ ДОРИСОВАНО] Схема эксперимента

2.6 Теоретические расчеты

Глава 3

Результаты и обсуждение

3.1 Получение и первичная обработка данных

1D или 2D На рис. 3.1 можно увидеть типичные снимки, полученные в сканирующем эксперименте.

3.2 Вычитание фона, аппроксимация пиков

Распознавание кристаллических пиков и аморфного фона производилось с помощью алгоритма "Rolling ball".
Принуип действи понятен из рис. 3.2

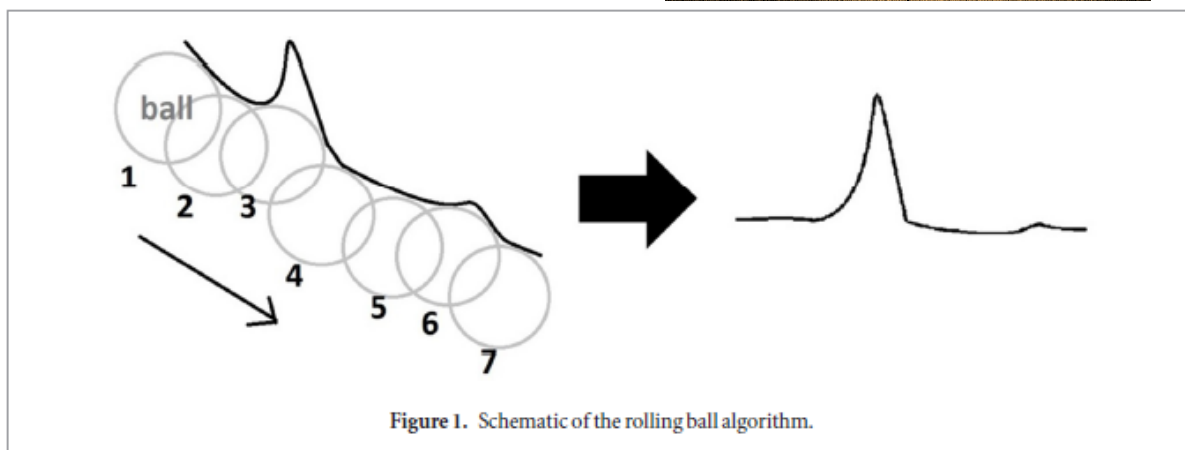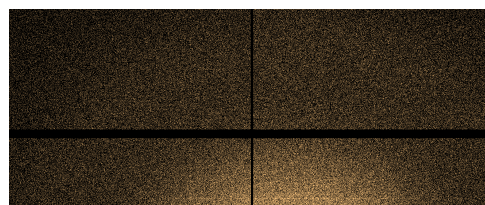

Figure 1. Schematic of the rolling ball algorithm.

Рис. 3.2: Caption

Данный алгоритм применяется при анализе данных рентге-

новской дифракции, рамановской спектроскопии и пр. []. Как правило он применяется к двумерным дифрактограммам кристаллических материалов, как например, в работе [10]. Однако подходящая реализация для одномерных профилей, необходимая в случае дифракции на полимерах, не представлена в открытых источниках.

Ниже (листинг 3.1) приведена адаптация алгоритма из работы [1], реализованная на языке Python.

```python
import numpy as np

def incmatrix(genl1, genl2):
    m = len(genl1)
    n = len(genl2)
    M = None #to become the incidence matrix
    VT = np.zeros((n*m,1), int)  #dummy variable

    #compute the bitwise xor matrix
    M1 = bitxormatrix(genl1)
    M2 = np.triu(bitxormatrix(genl2),1)

    for i in range(m-1):
        for j in range(i+1, m):
            [r,c] = np.where(M2 == M1[i,j])
            for k in range(len(r)):
                VT[(i)*n + r[k]] = 1;
                VT[(i)*n + c[k]] = 1;
                VT[(j)*n + r[k]] = 1;
                VT[(j)*n + c[k]] = 1;

                if M is None:
                    M = np.copy(VT)
                else:
                    M = np.concatenate((M, VT), 1)

                VT = np.zeros((n*m,1), int)

    return M
```

Листинг 3.1: Python example

3.3 Карты кристалличности

3.4 Параметры решетки, расчеты

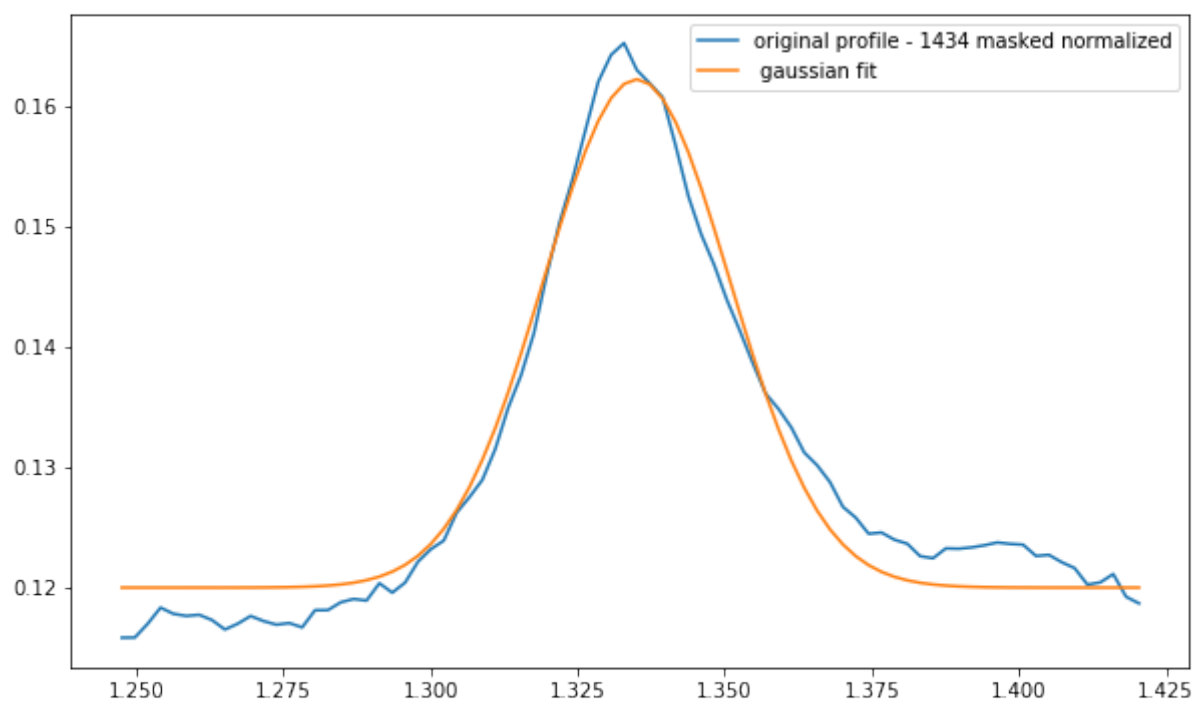**Rolling-ball** погрешности, чем хорошо, почему он, какие еще бывают

Рис. 3.3: Аппроксимация формы пика по разным моделям

фиттинг

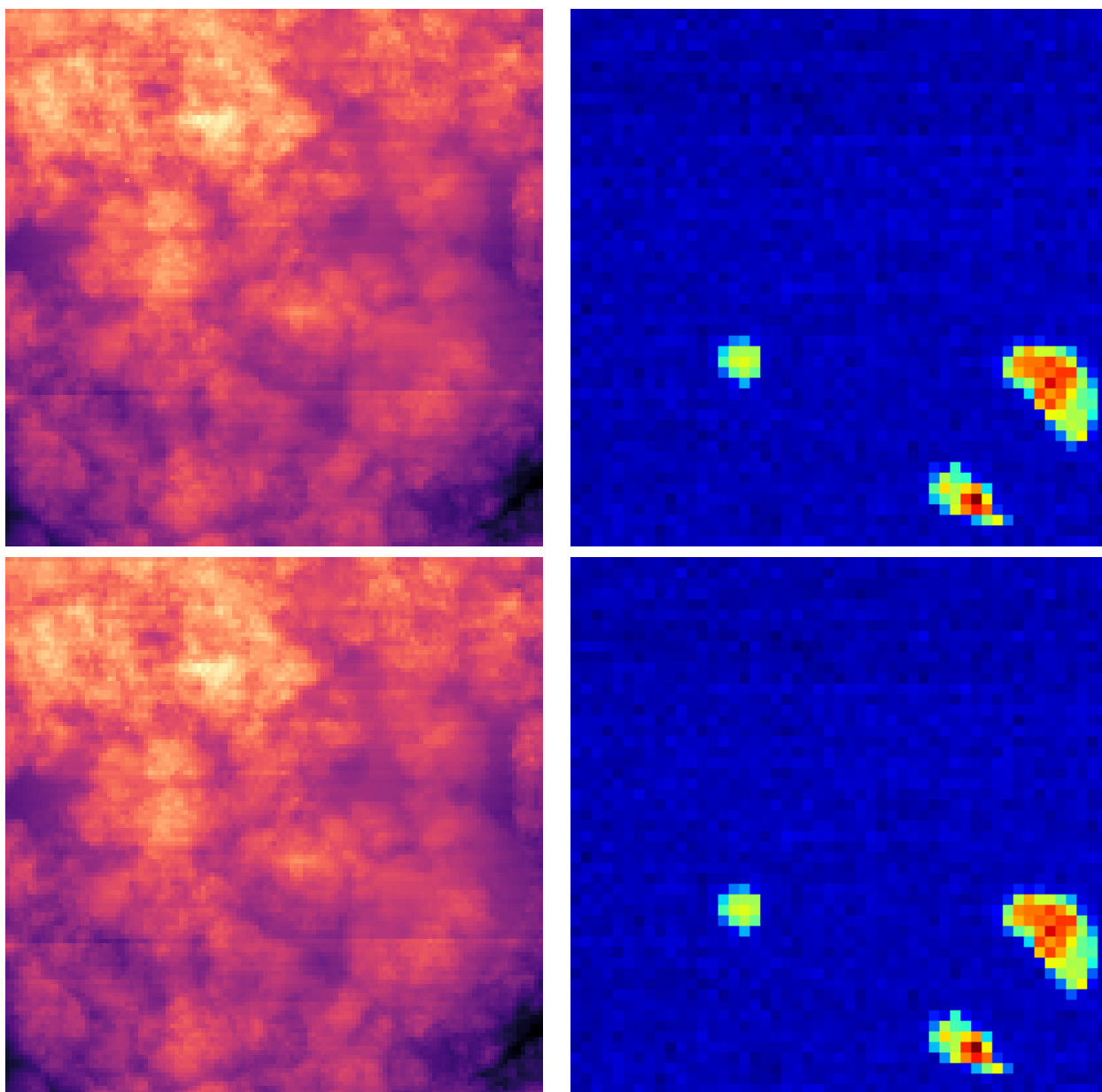**Карты кристалличности**   Свойства и результаты прочих исследований: [Vaganov corrected]

Рис. 3.4: Карты кристалличности

Заключение

3.5 Список результатов

3.6 Планы на будущее

СЛС можно делать с композитами, котрые на нейлоне показали улучшение механических свойств и уменьшение пористости [7]

Вроде как есть проблемы с тем, чтоб ыполучить композитный порошок нормальной формы [4]

3.7 Благодарности

Список литературы

[1] A. Kneen, «Algorithm for fitting xrf, sem and pixe x-ray spectra backgrounds», Nucl. Instr. Meth. Phys. Res. B, 209—213 (1996).

[2] Ю. Михайлин, *Термоустойчивые полимеры и полимерные материалы* (Профессия, 2006).

[3] V. E. Y. et al., «Morphology and mechanical properties of carbon fiber reinforced composites based on semicrystalline polyimides modified by carbon nanofibers», Composites A **39**, 85—90 (2008).

[4] R. G. et al., «Processing of a polyamide-12 carbon nanofibre composite by laser sintering», Polymer Testing **30**, 94—100 (2011).

[5] R. H. R.D. Goodridge C.J. Tuck, «Laser sintering of polyamides and other polymers», Progress in Materials Science (2011).

[6] J. C. Lin Dong Nicolas Barth и S. Ahzi1, «Modeling and numerical simulation of selective laser sintering», в Eurosime (2016).

[7] W. Jing, «Surface modification of carbon fibers and the selective laser sintering of modified carbon fiber nylon 12 composite powder», Materials and Design **116**, 253—260 (2017).

[8] S. Josupeit и H.-J. Schmid, «Experimental analysis and modeling of local ageing effects during laser sintering of polyamide 12 in regard to individual thermal histories», Journal of Applied Polymer Science **134** (2017).

[9] S. C. Ligon, «Polymers for 3d printing and customized additive manufacturing», Chem. Rev. **117** (2017).

[10] Y. Z. et al, «A novel method to remove the background from x-ray diffraction signal», Phys. Med. Biol. **63** (2018).

[11] S. T. Mohammed Arif P. Nandakumar Kalarikkal, «Crystallization in multiphase polymer systems», в (2018) гл. 1.

[12] N. S. Murthy, «Crystallization in multiphase polymer systems», в (2018) гл. 3.

[13] Г. В. В. В. Е. Юдин, «Полиимидные порошки для 3d-печати по методу СЛС», ПОЛИМЕРНЫЕ МАТЕРИАЛЫ И ТЕХНОЛОГИИ **4** (2018).