ORIENTATION DOWNLOAD OF POLYCAPROLACTAM. I. PRIMARY STRUCTURES

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ABSTRACT

It was investigated the possibility for production of suitable for orientation download primary structures of polycaprolactam. Depending on the degree of super cooling during compression have been received fundamentally different initial isotropic structures of polycaprolactam thin films. It was found that most suitable for orientation download is the fine spherulitic morphology.

Keywords: polycaprolactam, orientation download, primary structures, treatment.

INTRODUCTION

The orientation uniaxial download [1-3] of flexible chain fiber and foil forming polymers leads to improvement of their modular strength and mechanical properties in a desired direction. This result is achieved through the repackaging of the macromolecular chain segments simultaneously accompanied by a formation of a proper orientation. The effectiveness of such a structural reorganization depends mainly on the rheological properties of the primary polymer structure, and of the conditions and extent of the non-destructive orientation download. Usually the mechanical characteristics improving in the operating-oriented state directly and proportionately depends on the primary structure and from its withdrawal conditions, too. Therefore it can be argued that the necessary and sufficient condition for optimizing of the orientation download is to optimize the conditions for forming and download of the starting polymer structure. Ie, to find a science-based options to maximize of the mechanical behavior on the flexible chain polymers in oriented state is the finding of a mutually suitable structures and conditions for their orientation downloading. On one side, finding of suitable conditions for the formation of appropriate starting isotropic structure [4-12]. Structure with a good deformability to achieve of maximum possible for a given polymer, non-destructive levels of Orientation download. On the other hand, finding of suitable conditions for achievement of maximum possible for the given polymer non-destructive levels of orientation download. Each structure requires the appropriate conditions for optimal downloading and specified downloading conditions are optimally suitable only for a single corresponding structure.

All of the above noted is particularly important in polycaprolactam not only because of its great industrial production and wide application, mainly in oriented state. First of all polycaprolactam (PCL) is a model fiber forming flexible chain polymer, synthetic polyamide analogue of the important class of natural biopolymers - polypeptides. As such, the study of the optimization of its orientation drawing, and in particular the clarification of the mechanisms and

kinetics of the deformation processes and repackaging of the macro molecular chain segments in the amorphous and crystalline phase are a direct opportunity to access some inaccessible processes in the living nature. But even if we exclude some similar perspectives it is sufficiently attractive the prospect to studying the rich polymorphism underlying the structural reconstruction at PCL orientation download, as a model in the forming hydrogen bonds (H-bonds) flexible chain polymers. Therefore, namely, the actuality of studying the possibility of optimizing its orientation download is indisputable.

EXPERIMENTAL

There are used different modes polycaprolactam (PCL-1 with $\eta_{rel.\ 1\%\ sol.\ H2SO4} = 2.64$; $W_{mass.\%} = 1.0$ and PCL-2 with $\eta_{rel.\ 1\%\ sol.\ H2SO4} = 2.32$; $W_{mass.\%} = 0.01$) with different molecular masses and molecular-mass distribution (characteristic viscosity in 1% solution of H_2SO_4 $\eta_{rel} = 2.11 \div 2.83$), contents of low-molecular tie in the interval $1.0 \div 12.0$ % mass, moisture content from 0.1 to 0.01 % mass, as a necessary condition about the obtaining of crystal structures with different perfection. There are formed thin folios in a large diapason of forming conditions: $T_{pr.} = 483 \div 513$ K and $T_c = 77 \div 473$ K. The high temperature X-ray investigations are carried out by repeated cyclical heating and cooling in the temperature interval from 293 K to 513 K with heating rate of 5 K/min and 5 min tempering for every scanned temperature at interval of 5 K. The initial isotropic structure of the pressed folios was characterized by light-microscopy, electron-microscopy and with powder X-ray diffraction methods using a polarization light-microscopy Amplival Pol, Karl Zeiss, Jena, Germany, SEM BS – 340, Tesla, Brno, Cheh Republic, TEM Opton 10B, Feintechnik, Oberkochen, Germany. Using an universal powder X-ray diffractmeters URD 6 ("Präzisionsmechanik – Freiburg", Germany) and URD 3 (DRON 3) equipped with a high temperature chamber UVD 2000 ("Burevestnik – Sankt Peterburg", Russia), at applying of CuKα radiation (β-filtered by Ni filter, λ = 1.5418 Å) there are obtained low- and high-temperature X-ray diffraction curves under different time/temperature conditions of simultaneous modification. The crystal phase perfection was defined by the packing compactness of the macromolecular chain segments in the crystal phase of the α-crystal modification [13]. The deformation/strength investigations are carried out at different temperatures by an apparatus "Tiratest – 2200", "Türinger Industriewerk", Rauenstein, Germany.

DISCUSSION

To achieve the objective of the PCL orientation download and namely the obtaining of high modular and high strength polymer materials as a result of nondestructive orientation structural reorganization, it is clear that is recommended the optimization of the nondestructive download conditions to be applied on suitable starting isotropic structures. I.e. initial structures having easy unravel and foldable macromolecular chain segments and appropriate molecular-mass distribution of the supporting load during download segments connections. Structures which possess high density and low micro-heterogeneity. Structures with fine spherulitic morphology

and robust boundaries between the different phases. Due to the low density and highly intertwined chain segments the highly amorphied supercooled melts are not these structures. Maximum isothermal crystallized structures are not the most convenient and preferred for optimal Estimate download. They have a maximum specific density and good pre-packaging segment but assume too precise, practically difficult to implement technological conditions of the untangling of the crystalline phase when downloading.

Similar raw isotropic structures are especially vulnerable to high orientation tensions due to the low density of the supporting segments-connections in the inter-phase amorphous areas between morphological elements. These are large PCL spherulitic structures with high total degree of crystallinity and of the crystalline phase perfection. Namely these are the isothermal crystallized phases. They are characterized by a large micro, submicro and nano-heterogeneity, with weak boundaries between phases and a strong separation of the fractional distribution in size of the chain segments in the amorphous regions. In such structures the alternative destructive processes during uniaxial downloads loading may prevail over the orientation ones.   It   is logical to assume that the best optimal for an orientation download are isotropic PCL structures with complex polymorphic composition, medium degree of crystallinity and perfection of the crystalline phase formed during extrusion of thin films or molding fibers. Such fibers possess a rich polymorphic structure and combination of intermediate mesophases in different proportions. Such structural mixtures are natural combination of all basic packages of the chain segments in the polymer volume. In them are realized all possible real structural conditions that determine the material density depending on the degree of the melt super cooling. Such structures are most suitable for deformation structural reorganization in the widest range of conditions. In them always have proper enough weakly packed regions from which to start destructive thermo-mechanically initiated uni-axial deformation at the corresponding low enough orientation tensions. With the deformation development under rich enough structural diversity, in a natural way enriched the load-bearing factions of segments-links in length and degree of tautness and respectively of intensity.

In the deformation process gradually include close in location, structure and terms of download polymer volumes, increasing self-consistent the close each other micro-local orientation tensions. In a similar mechanism which will be discussed in detail in our subsequent work can be achieved higher levels of nondestructive PCL orientation download. However with this work it is mainly aimed to clarify the conditions for the creation of a sufficiently rich structural diversity and their characterization by some determining their deformability structural characteristics. In general, the basic direct measure of the materials deformability is the mechanical modular characteristics. But when it comes to uni-axial orientation nondestructive deformation more informative is the direct real structural, unlike from the related mechanical information that does not always allow adequate forecasts. This is because the deformation process is connected to a permanent structural reorganization, respectively permanently modification of the mechanical behavior. In deformation process any current and future structural

condition is clearly directly related to the preceding.

Furthermore, the development of the deformation process mainly depends on the defectiveness of the different structural levels, as well as the micro heterogeneity, the segment package density at the nano level, macro molecular atomic molecular level. This is the so-called crystallographic structural level in the crystallizable flexible chain polymers or more - their fine crystalline structure. Their crystal structure determined the morphology, micro and macro structural characteristics which are directly related to their mechanical behavior. Therefore, due to the inability for determination of all structural and mechanical properties determining the nondestructive PCL thin films deformation during their orientation download we have chosen only some basic of them. As particularly informative, determining the mechanism and development of deformation processes we determined the morphological elements dispersity and quality of the boundaries between them, i.e. the morphological specifics of the objects. Also we identified the underlying crystallographic specificity, i.e. polymorphic composition of the tested structures. And of course, we determined the formation conditions of the structures, as well as the type and purity of the used polymer. Part of the required information is provided in Table. 1.

In table. 1 are present experimental results obtained of the studies on the possibility to create enough variety of PCL isotropic structures providing of a good choice of comfortable ones to optimize the conditions for non-destructive PCL orientation download. The differing in viscosity and rheological characteristics PCL-1 and PCL-2, especially at different temperatures of the melt and the degrees of super cooling during crystallization at different temperatures and cooling rates after compression of the thin foils, forming radically different structures from crystallographic and morphological viewpoints. This is evident as from the general degree of crystallinity α_c, and from the polymorphic composition of the crystalline phase. The quantity proportion of the different crystal forms in the PCL crystalline phase is sure indication of its mechanical resistance and the mechanism of its deformability and predisposition to different modes and degrees of uniaxial deformation orientation download.

The various crystallographic modifications are characterized by a different type and density of the segment pack in the crystalline phase, different deformation resistance and modular features at various schemes of mechanical stresses applying. Furthermore, the packaging of the segments in the crystalline phase to a large extent determines the structure of amorphous regions. Especially in dependency and from the packing density

Table 1. Technological molding conditions and structural characteristics of the source for orientation download PCL isotropic structures formed into thin films of 50 μ.

№	Object	T_{ex}, °C	T_{cr}, °C	$(T_{ex} - T_{cr})^*$, °C	$(T_{ex} - T_{cr})/\tau^{**}$, °C/s	α_c, %	Polymorphism α:β:γ:δ, %	Polymorphic transitions	Packaging density of MMCS, %	Crystal phase perfection, %	Morphology
1	′PCL-1[1]	220	200	20	20	78,3	76:19:2:3	α↔β↔γ↔δ	97	98	Large spherulitic with a wide distribution
2	′PCL-1[2]	220	20	200	200	32,1	39:41:8:12	α↔β↔γ↔δ	74	95	Medium spherulitic with medium distribution
3	′PCL-1[3]	220	0	220	220	11,2	18:12:46:24	α↔β↔γ↔δ	61	93	Fine spherulitic with narrow distribution
4	′PCL-1[4]	220	-93	313	313	2,7	5:4:37:54	α↔γ↔δ	57	90	Fine spherulitic with narrow distribution
5	′PCL-1[5]	220	-196	416	416	1,8	1:2:32:65	α↔γ↔δ	57	88	Fine spherulitic with narrow distribution
6	″PCL-1[1]	230	200	30	30	78,9	79:16:2:3	α↔β↔γ↔δ	98	99	Large spherulitic with a wide distribution
7	″PCL-1[2]	230	20	210	210	33,3	40:40:9:11	α↔β↔γ↔δ	76	96	Medium spherulitic with medium distribution
8	″PCL-1[3]	230	0	230	230	11,4	18:12:43:27	α↔β↔γ↔δ	62	94	Fine spherulitic with narrow distribution
9	″PCL-1[4]	230	-93	323	323	2,9	5:4:36:55	α↔γ↔δ	58	90	Fine spherulitic with narrow distribution
10	″PCL-1[5]	230	-196	426	426	1,6	1:2:34:63	α↔γ↔δ	56	89	Fine spherulitic with narrow distribution
11	‴PCL-1[1]	240	200	40	40	79,2	78:17:3:2	α↔β↔γ↔δ	99	99	Large spherulitic with a wide distribution
12	‴PCL-1[2]	240	20	220	220	34,3	41:42:8:9	α↔β↔γ↔δ	78	97	Medium spherulitic with medium distribution
13	‴PCL-1[3]	240	0	240	240	11,5	16:9:46:29	α↔β↔γ↔δ	63	95	Fine spherulitic with narrow distribution
14	‴PCL-1[4]	240	-93	333	333	3,0	6:6:35:53	α↔γ↔δ	59	91	Fine spherulitic with narrow distribution
15	‴PCL-1[5]	240	-196	436	436	1,9	3:2:31:64	α↔γ↔δ	57	90	Fine spherulitic with narrow distribution
16	′PCL-2[1]	220	200	20	20	77,3	77:20:1:2	α↔β↔γ↔δ	97	99	Large spherulitic with a wide distribution
17	′PCL-2[2]	220	20	200	200	30,1	40:40:9:11	α↔β↔γ↔δ	74	96	Medium spherulitic with medium distribution
18	′PCL-2[3]	220	0	220	220	12,2	19:13:44:24	α↔β↔γ↔δ	62	93	Fine spherulitic with narrow distribution
19	′PCL-2[4]	220	-93	313	313	2,9	5:4:38:53	α↔γ↔δ	56	90	Fine spherulitic with narrow distribution
20	′PCL-2[5]	220	-196	416	416	1,7	2:2:32:64	α↔γ↔δ	57	89	Fine spherulitic with narrow distribution
21	′PCL-2[1]	230	200	30	30	77,7	80:16:2:2	α↔β↔γ↔δ	98	99	Large spherulitic with a wide distribution
22	″PCL-2[2]	230	20	210	210	32,8	41:39:9:11	α↔β↔γ↔δ	75	96	Medium spherulitic with medium distribution
23	″PCL-2[3]	230	0	230	230	11,8	19:14:42:25	α↔β↔γ↔δ	63	94	Fine spherulitic with narrow distribution
24	″PCL-2[4]	230	-93	323	323	2,9	5:5:35:55	α↔γ↔δ	58	91	Fine spherulitic with narrow distribution
25	″PCL-2[5]	230	-196	426	426	2,0	2:3:34:61	α↔γ↔δ	57	90	Fine spherulitic with narrow distribution
26	‴PCL-2[1]	240	200	40	40	77,2	79:18:2:1	α↔β↔γ↔δ	99	99	Large spherulitic with a wide distribution
27	‴PCL-2[2]	240	20	220	220	35,1	43:45:6:6	α↔β↔γ↔δ	79	97	Medium spherulitic with medium distribution
28	‴PCL-2[3]	240	0	240	240	12,0	19:8:45:28	α↔β↔γ↔δ	65	95	Fine spherulitic with narrow distribution
29	‴PCL-2[4]	240	-93	333	333	3,4	8:7:36:49	α↔γ↔δ	59	92	Fine spherulitic with narrow distribution
30	‴PCL-2[5]	240	-196	436	436	2,2	4:4:32:60	α↔γ↔δ	58	90	Fine spherulitic with narrow distribution

Note: 1. If at first approximation we assume that due to the mutual influence both the low thermal PCL conductivity and the small thickness of the objects the time of the structure forming is about one second, then the cooling rate** and the degree of supercooling* are equal to the difference between the extrusion temperature (melt temperature) and the crystallization temperature (cooling temperature); 2. The coexistence of the PCL main crystal forms in different quantitative ratio and the possible temperature-initiated polymorphic transitions between them determine the different packaging density and the crystalline phase perfection in the real complex isotropic structures for orientation; 3. The crystallography of the fine crystalline structure is related to the morphology and the deformability of the initial for orientation download isotropic structure, by the package density and its perfection.

Volume VI, 2016, Number 4: TECHNICAL STUDIES

and the crystalline phase perfection. Usually by our unpublished data the high amount of content of the crystalline form and generally of the crystalline phase determines its higher density packaging and perfection. This is a precondition for the formation of strained small amorphous regions in comparison with the same degree of crystallinity, but lower perfection of the crystalline phase. Typically the crystalline phase perfection is related to the higher content of the stable PCL alpha form although any other shape can be characterized with different perfection correlating to its quantity in the simultaneous polymorphic mixture. The analysis of the presented experimental results showed that the high speeds and degrees of the melt super cooling during extrusion of thin films 50 μ leads to amorphizing of the obtained isotropic structures. Larger degrees of super cooling (deep hardening) lead to stronger amorphization. In the deepest hardening these effects are nonlinear, possibly due to the low coefficient of PCL thermal conductivity. At low degrees of super cooling is possible to achieve over 70% total crystallinity. This is aided by the polymer type (a good rheological characteristics, low viscosity and low molecular weight plasticising effect of the compounds), the higher temperatures of pressing and cooling during the formed structures fixing. The complex impact of the various factors, however do not always lead to unambiguous predictions and the logically expected results. Within the present experiment, the highest total degree of crystallinity of $\alpha_c = 79.2\%$ is obtained for PCL-1, at extrusion temperature of $T_{ex.} = 240^0C$ and cooling temperature $T_{cr.} = 200^0C$. As is mentioned above, in addition to the total PCL degree of crystallinity of particular importance is the polymorphic composition of the crystalline phase and quantifying presence of the alpha form which depend the packing density and its perfection. Of course, at the initial stage and during the orientation download is desirable the predominant presence of the more deformable, mechanically more unstable transitional γ-crystalline form. This crystallographic modification provides such a package of the chain segments which can be easily transformed into transitional β and stable α-crystal form. From Table. 1 it is seen that the preferred γ-form (about 46%) with a sufficient amount of super cooled melt δ-shape consisting of a large percentage mesophases (mainly smectic because of the fixing intermolecular distances hydrogen bonds) is formed for PCL-1 under conditions of moderate (soft) hardening around 0^0C. Such structures allow the realization of all possible polymorphic transitions in the crystalline phase in the volume of the polymer. Therefore facilitate the running of nondestructive orientation download under influence of self-consistent load implemented under various schemes which providing low enough safety orientation tensions. Such structures show morphology with a relatively low micro-heterogeneity in the packing density of the chain segments in both the crystalline and amorphous phases in. Especially important to them is the lack of clear, inter-phase boundary between the especially big morphological elements.

Such clearly defined borders at the structures with a high degree of crystallinity

play the role of major structural defects deteriorating the mechanical behavior of the objects in both the isotropic and the oriented state. They do not allow the achievement of high levels levels of uniaxial deformation and prevent the realization of destructive orientation download.

CONCLUSION

1. Suitable and convenient for holding of optimal destructive orientation download are isotropic slightly hardened structures of not extracted from low molecular weight compounds polycaprolactam with a low micro heterogeneity.These are fine spherulitic structures having similar in size morphological elements without clear inter-phase boundary between them.

2. Such isotropic structures of polycaprolactam have a low total degree of crystallinity about 15% and predominantly content of easily deformable transient gamma form. Such starting isotropic structures have a relatively low density of the segment package and the crystal phase perfection and at heat mechanical modification showed a tendency of realization of all possible polymorphic transitions in the polymer volume.

3. The obtaining of such isotropic structures is possible via compression molding of thin polycaprolactam films about 50 μ with pressing temperatures which are in conformity with the PCL thermal stability up to 240^0C and relatively moderate cooling rates and degrees of hypothermia (about 200-240^0C).

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