ORIENTATION DOWNLOAD OF POLYCAPROLACTAM. II. OPTIMIZATION OF THE ORIENTATION CONDITIONS

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ABSTRACT

It was investigated the possibility for optimizing the conditions for orientation download of different initial structures of polycaprolactam. The advantages of the gradual multi-stage downloading are shown.

Keywords: *polycaprolactam, orientation download, technological conditions, optimization*

INTRODUCTION

In the first part of the present work devoted to the polycaprolactam (PCL) orientation download optimizing [1-8, 19, 20] we introduced the necessity of finding of mutual suitable structures and conditions for their withdrawal. There were discussed the possibilities for obtaining of a wide variety of radically different isotropic structures, depending on the thin films molding conditions and especially on the degree of super cooling during crystallization after pressing. It was defined a system of criteria for suitability assessing of the different structures for maximum non destructive PCL orientation download under the most comfortable technological conditions. The purpose of the present notice is to optimize the conditions for withdrawal Estimate selected isotropic raw structures.

We showed that an appropriate way to solve the problem includes selecting from the prepared variety of raw structures of appropriate structures with good non-destructive deformability, followed by planned optimization of their withdrawal conditions. It is recommended the multifactorial planning to be based on model mechanisms of the structural reorganization in uni-axial non destructive elastic and plastic deformations of polycaprolactam (PCL). These mechanisms must be secured by experimentally confirmed criteria for evaluation, comparison and analysis of the complex simultaneous interaction of the structural elements and the most elementary processes between them.

EXPERIMENTAL

There are used different modes polycaprolactam (PCL-1 with $\eta_{\text{rel. 1\% sol. H2SO4}} = 2.64$; $W_{\text{mass.\%}} = 1.0$ and PCL-2 with $\eta_{\text{rel. 1\% sol. H2SO4}} = 2.32$; $W_{\text{mass.\%}} = 0.01$) 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 ÷ 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, $\lambda = 1.5418$ 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 [11-18, 21]. The deformation/strength investigations are carried out at different temperatures by an apparatus “Tiratest-102”, Germany.

DISCUSSION

In previous studies [9,10] we found the easily but not effective enough orientation download of strong amorphied PCL isotropic structures and markedly more successful, but very difficult to achieve maximum nondestructive orientation downloading of such objects with high degree of crystallinity. Significantly more convenient and efficient enough is the realization of orientation downloading of structures formed under conditions close to the convenient technological at $T_{cool.} \sim 20^0$C with degree of crystallinity $\alpha_c = 15 \div 30\%$ or less hardened at $T_{cool.} \sim 0^0$C with degree of crystallinity $\alpha_c = 10 \div 15\%$. However, for optimizing the orientation downloading that is not enough. It is necessary to find not of the most comfortable but the most effective conditions for achieving the highest possible degree of destructive orientation downloading corresponding to the maximum modular and strength characteristics of PCL in oriented state. As a presumption, it is possible for structures of high density, such as those with a high degree of crystallinity. To achieve of greater levels of downloading is needed the greatest mass of the more compacted materials crystallized with tightly packed in the crystalline phase macromolecular chain segments. Their non-destructive "untangling" stretching and orientation arrangement during the uniaxial downloading is difficult and "capricious" work, but the improvement of the operating mechanical behavior in oriented state as a result of such structural reorganization worth the effort. The big difficulty is the fact that the degradation of tightly packed crystalline phase with purpose of untangling, stretching and stacking of the macromolecular chain segments are needed increased efforts and temperatures. Due to the thermal fluctuation nature of the destruction both factors stimulate it strongly.

Therefore, it is necessary to observe simultaneously many conditions, namely: Suitable mechanically resistant non defective homogeneous structure, not too high temperatures and mechanical stresses, agreed with the relaxation spectrum loading speeds and many other small but important details which must simultaneously to be met. They can not be met in one single act of downloading from isotropic to the final operating oriented condition. In order to be download non destructive and maximum successful it should be phased with gradually increasing of the load or gradually with a gradual increase of the temperature. Or combined with the simultaneous compliance with these two basic principles. Then the download is slower and less brutal and destructive to the material. At each new level (with a gradual increase of the temperature) and stage (with gradually increasing of the load) the material is more ready, structurally reinforced by the previous structural heat mechanical modification and incur more non destructive the next. In this manner it is possible with a weak, non-destructive increasing of the deformation load and respectively the orientation stresses to achieve higher levels of non destructive download and the related improvement of the mechanical properties. Without increasing of the orientation stresses even in their reduction at any subsequent stage (with increasing temperature of the download) more deformable at a high temperature material, gradually but non destructive is extended, orientate and strengthens.

The important thing is through self-regulatory way to be select, approbate and optimize the temperature-temporary parameters and the loading. With the correct selection of the increasing temperatures is possible by lowering of the orientation tensions due the reducing dimensions of the studied objects to optimize the orientation non destructive downloading to afford better final exploitation results. In the same way it may proceed and with the temperature at a specified load within a given stage as well as with the loading at a given temperature within the respective level of downloading. Furthermore the orientation tensions and the speed of uniaxial deformation are self regulated according to the downloading temperature under gravitational downloading (with constant load). And on involuntary downloading self regulating are the tensile load (respectively, again the oriented stresses) and the predetermined download speed, again depending on the temperature of the process. All of this is specific to each different structural organization and it is best to approbate by the method of trial and error. Therefore the experiment is precise and laborious.

Usually within the main PCL structural organizations the degrees of orientation downloading are three. At 110, 140 and 170^{0}C but they can be up to five. At 100, 120, 140, 160 and 180^{0}C, but at the last temperature the non destructive operation of the process is controlled very difficult. Within each temperature (degree of downloading) optimally are implemented two stages. Within each stage at the gravitational load, for example, can be approbate stepwise download (bidirectional cyclic repetition through the heat element for gradient heating with a structural fixing of the objects when downloading) up to reaching of constant deformation. The gradient heat element-retainer implement the principle of Zhurkov [3,4] for a minimum stay of loaded materials and objects at high temperature, due to the thermal fluctuation character of destruction process according to the kinetic theory. The heating element-retainer is a double point heater with one-sided asymmetric gradient radiator and on the other side of the sandwich principle quench cooler-retainer.

The table illustrates the optimization approach to non destructive orientation downloading, observing the principle of control and feedback of the polymorphic composition and the possible thermo mechanically initiated polymorphic transitions as a measure for optimal, natural and safe measure for deformability of the materials under the relevant technological conditions. The fibrillar morphology from the final chapter is one of the criteria illustrating the discrepancy between the level of download and the deformation of the spherulites in macro fibrils during the orientation. Ie, the lack of conformity and proportionality between the level of downloading, elastic, plastic deformation, quantitative ratios of the orientation and destructive processes in uniaxial deformation. There, precisely, are the reserve resources to optimize the orientation download.

Table 1. Structural and mechanical properties of thin PCL foils subjected to gradually orientation download.

№	Initial isotropic state			Gradually high temperature uniaxial orientation with gradient heating of the objects and permanent fixation of the intermediate structures												fibrillar morpho-logy, d/l
				I stage - 110^{0}C				II stage - 140^{0}C				III stage – 170^{0}C				
	Object	α_c, %	Polymorphism, α:β:γ:δ, %	λ	E, MPa	$\sigma_{ten.}$ MPa	Polymorphic transitions	λ	E, MPa	$\sigma_{ten.}$, MPa	Polymorphic transitions	λ	E, MPa	$\sigma_{ten.}$, MPa	Polymorphic transitions	
1	′PCL-1^{1}	78,3	76:19:2:3	3,3	365	175	α↔β↔γ	5,5	720	335	α↔β↔γ	6,5	1080	501	α↔β↔γ	0.185
2	′PCL-1^{2}	32,1	39:41:8:12	3,1	340	179	α↔β↔γ↔δ	5,1	681	366	α↔β↔γ↔δ	6,6	1021	549	α↔β↔γ↔δ	0.185
3	′PCL-1^{3}	11,2	18:12:46:24	2,9	325	186	δ↔γ↔β↔ α	5,0	649	375	δ↔γ↔β↔ α	6,6	974	563	δ↔γ↔β↔ α	0.182
4	′PCL-1^{4}	2,7	5:4:37:54	2,8	315	188	δ↔γ↔β↔ α	4,8	632	390	δ↔γ↔β↔ α	6,4	947	575	δ↔γ↔β↔ α	0.185
5	′PCL-1^{5}	1,8	1:2:32:65	2,8	309	189	δ↔γ↔β↔ α	4,7	621	388	δ↔γ↔β↔ α	6,3	931	574	δ↔γ↔β↔ α	0,189
6	″PCL-1^{1}	78,9	79:16:2:3	3,3	368	176	α↔β↔γ	5,6	739	349	α↔β↔γ	6,6	1008	524	α↔β↔γ	0,182
7	″PCL-1^{2}	33,3	40:40:9:11	3,2	370	179	α↔β↔γ↔δ	5,2	741	358	α↔β↔γ↔δ	6,7	986	537	α↔β↔γ↔δ	0,182
8	″PCL-1^{3}	11,4	18:12:43:27	3,0	365	182	δ↔γ↔β↔ α	5,1	728	361	δ↔γ↔β↔ α	6,6	1092	542	δ↔γ↔β↔ α	0,182
9	″PCL-1^{4}	2,9	5:4:36:55	2,9	335	187	δ↔γ↔β↔ α	4,9	674	372	δ↔γ↔β↔ α	6,4	1011	558	δ↔γ↔β↔ α	0,185
10	″PCL-1^{5}	1,6	1:2:34:63	2,8	319	189	δ↔γ↔β↔ α	4,9	642	377	δ↔γ↔β↔ α	6,4	963	565	δ↔γ↔β↔ α	0,185
11	‴PCL-1^{1}	79,2	78:17:3:2	3.4	369	179	α↔β↔γ	5,6	738	359	α↔β↔γ	6,5	1112	539	α↔β↔γ	0.182
12	‴PCL-1^{2}	34,3	41:42:8:9	3,3	370	174	α↔β↔γ↔δ	5,3	737	349	α↔β↔γ↔δ	6,6	1105	524	α↔β↔γ↔δ	0.182
13	‴PCL-1^{3}	11,5	16:9:46:29	3,1	367	181	δ↔γ↔β↔ α	5,1	731	364	δ↔γ↔β↔ α	6,6	1096	546	δ↔γ↔β↔ α	0.182
14	‴PCL-1^{4}	3,0	6:6:35:53	2,9	344	186	δ↔γ↔β↔ α	5,0	692	375	δ↔γ↔β↔ α	6,4	1038	556	δ↔γ↔β↔ α	0,189
15	‴PCL-1^{5}	1,9	3:2:31:64	2,9	326	186	δ↔γ↔β↔ α	4,9	659	371	δ↔γ↔β↔ α	6,3	989	557	δ↔γ↔β↔ α	0,189
16	′PCL-2^{1}	77,3	77:20:1:2	3.4	372	179	α↔β↔γ	5.7	747	380	α↔β↔γ	6,8	1123	540	α↔β↔γ	0,179
17	′PCL-2^{2}	30,1	40:40:9:11	3,2	347	182	α↔β↔γ↔δ	5,4	698	366	α↔β↔γ↔δ	6,8	1045	549	α↔β↔γ↔δ	0,175
18	′PCL-2^{3}	12,2	19:13:44:24	2,9	320	186	δ↔γ↔β↔ α	5,1	647	368	δ↔γ↔β↔ α	6,8	971	552	δ↔γ↔β↔ α	0,179
19	′PCL-2^{4}	2,9	5:4:38:53	2,9	310	188	δ↔γ↔β↔ α	5,0	627	379	δ↔γ↔β↔ α	6,6	940	569	δ↔γ↔β↔ α	0,182
20	′PCL-2^{5}	1,7	2:2:32:64	2,8	307	188	δ↔γ↔β↔ α	5,9	618	380	δ↔γ↔β↔ α	6,4	927	570	δ↔γ↔β↔ α	0.185
21	‘’PCL-2^{1}	77,7	80:16:2:2	3.4	368	178	α↔β↔γ	5,8	641	354	α↔β↔γ	7,0	962	524	α↔β↔γ	0,172
22	″PCL-2^{2}	32,8	41:39:9:11	3,2	375	179	α↔β↔γ↔δ	5,5	741	357	α↔β↔γ↔δ	7,9	991	535	α↔β↔γ↔δ	0,154
23	″PCL-2^{3}	11,8	19:14:42:25	3,0	369	183	δ↔γ↔β↔ α	5,5	736	366	δ↔γ↔β↔ α	7,6	1052	549	δ↔γ↔β↔ α	0,159
24	″PCL-2^{4}	2,9	5:5:35:55	2,9	344	186	δ↔γ↔β↔ α	5,2	689	375	δ↔γ↔β↔ α	7,1	1035	562	δ↔γ↔β↔ α	0,167
25	″PCL-2^{5}	2,0	2:3:34:61	2,9	332	189	δ↔γ↔β↔ α	5,1	671	377	δ↔γ↔β↔ α	7,0	1006	563	δ↔γ↔β↔ α	0,167
26	‴PCL-2^{1}	77,2	79:18:2:1	3,5	364	184	α↔β↔γ	5,8	722	369	α↔β↔γ	7,8	1083	554	α↔β↔γ	0,154
27	‴PCL-2^{2}	35,1	43:45:6:6	3,4	370	179	α↔β↔γ↔δ	5,4	734	363	α↔β↔γ↔δ	7,6	1101	551	α↔β↔γ↔δ	0,156
28	‴PCL-2^{3}	12,0	19:8:45:28	3,2	369	181	δ↔γ↔β↔ α	5,4	741	362	δ↔γ↔β↔ α	7,2	1112	543	δ↔γ↔β↔ α	0,164
29	‴PCL-2^{4}	3,4	8:7:36:49	3,0	354	187	δ↔γ↔β↔ α	5,2	712	373	δ↔γ↔β↔ α	7,1	1068	550	δ↔γ↔β↔ α	0,167
30	‴PCL-2^{5}	2,2	4:4:32:60	2,9	346	189	δ↔γ↔β↔ α	5,1	708	379	δ↔γ↔β↔ α	7,0	1062	552	δ↔γ↔β↔ α	0,167

Note: 1. Molding temperature (220^{0}C ’, 230^{0}C ‘’, 240^{0}C ‘’’) - ‘’‘ PCL-1 ^{1} - crystallization temperature (200^{0}C ^{1}, 20^{0}C ^{2}, 0^{0}C ^{3}, -93^{0}C ^{4}, -196^{0}C ^{5}); 2. Gradually high temperature uniaxial in stages cyclical orientation download with gradient heating of the objects and permanent fixation of the intermediate structures according to the kinetic thermal fluctuation nature of the strength and durability of the solids; 3. The fibrillar morphology expressed by the ratio of the diameter to the length of the fibrils should be equal to the reciprocal value of the total draw ratio at optimum keeping of the process; 4. The polymorphic transitions at different downloading stages are determined by the initial polymorphic composition and the drive to enrich the supporting fraction of segments connections and the stable alpha-form.

In Table 1 illustratively are presented results of carried orientation downloads of different starting isotropic structures in three-stage temperature-temporary schemes for optimization of the non destructive nature of the deformation process. They show, in general, the possibility for stepwise high temperature, predominantly orientation at the expense of the alternative predominantly destructive uniaxial downloading. Gradual in small steps at the expense of small safety levels of downloading at a slight increase or maintaining of the orientation stresses can be achieved larger final stages of downloading, determining better strain-strength characteristics. Any degree and the accompanying stages of non-destructive, "soft" optimized downloading increases by about 200% the relative deformation and allow the achievement of the end, about eight fold degrees of download 1123 MPa elastic modulus and 540 MPa tensile strength for optimal crystallized isotropic structures PCL.

CONCLUSION

Based on the obtained experimental results can be made the following key conclusions:

1. The optimization of the conditions for achieving of the maximum possible non destructive orientation download of PCL thin films with suitable starting isotropic structures consists in the finding of the corresponding most suitable temperature-time schemes for applying of self-regulatory with their specific uniaxial mechanical influences as a key element of the simultaneous complex stretching modification.

2. The optimal accordance of the temperature, time and mechanical characteristics of the process with the structural specificity of the studied objects ensures appropriate speeds of application of the mechanical stress and the realization of the needed non destructive orientation tensions to achieve the maximum possible and effective PCL orientation download.

3. According to the main criterion for optimal performed thermo mechanical modification in the form of non-destructive gradually high temperature uniaxial orientation download with gradient heating of the objects and gradually fixing of the structural reorganization, namely the mechanical behavior in the operating-oriented state, the optimization of the orientation process boils down not to a maximum download but to the most non-destructive carrying. It is shown the possibility of achievement at PCL of 1123 MPa elastic modulus and of 540 MPa tensile strength at degrees of download 6.8 (580% relative deformation) after three gradually (at 110^0C, 140^0C and 170^0C) two-stage (with approbation to raise orientation stress at each temperature) stepwise (with approbation of exhaustion of the deformation resource for the given conditions) and structural fixation download.

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