Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 6, Part 2

POLYPROPYLENE TAPES WITH CONTROLLED OPTICAL AND MECHANICAL PROPERTIES FOR THE "SMART'' PACKAGING

A.P. Kondratov, V. N. Buldyrev, I.N. Ermakova
Moscow State Ivan Fyedorov University of Printing Arts
2A, Pryanishnikova Street, 127550 Moscow

Abstract

There is detected the effect of an intensive light diffusion by transparent polypropylene tapes under an insignificant cyclic tension, which can be localized on a narrow tape zone and could be used for information recording. The information recording is realized by a short-time thermomechanical effect on stiff-elastic polypropylene. It is proposed by changing of the tape edge (narrowing) and local applying of high adhesion ink layers, using printing equipment, to get the "smart" package elements, which ensure its identification, counterfeit protection, control of storage temperature and shelf time. By method of a differential scanning calorimetry (DSC) the recording conditions are determined, and the mechanism and the optimal conditions of mechano-optical effect are investigated.

Key words: *"smart" packaging, tag, label, stiff-elastic polypropylene, light diffusion, differential scanning calorimetry (DSC)*

1. INTRODUCTION

The polypropylene films are wide used in the production of flexible packaging and various details of modern packaging for various mass consumption goods [1] on which the printed information and protective marking are applied by printing methods. The package printing, the making of protective construction units of these packing materials and the marking are connected by certain idea of designer and are directed on the solving of several important problems: the attraction of attention of consumers to the goods, information about the quality and the manufacturer of product, as well as about their authenticity and useful time. The visual demonstration of company packed product authenticity and the control of its originality by consumer's simple manipulations are taking on special significance in the unfair competition of manufacturers of original and counterfeit products. The verification tests should be easily realizable by any consumer without special background or experience of such tests directly in the sales area according the rules printed on the packaging using of standard techniques or organoleptical study.

As regards the foodstuffs and other mass consumption goods the application of organoleptical methods of authenticity identification of packaging is preferably; these methods are based on the application of packaging materials with special texture and mechanical properties or optical effects for counterfeit exception, as the consumers may assume. The development of packaging materials with special properties is an all-important problem of polygraphic material science.

Recently it was offered to use the films made of stiff-elastic polypropylene for production of counterfeit protected label and tags of various forms [2]. The offer is recognized as an invention and is assumed as a basis for some construction variants of flexible packaging protective elements made of polymeric materials protected by patents [3-5]. The new direction of counterfeit protection of goods and packaging, made of film materials is based on results of research and application of new mechano-optical effect of reversible transparency change of nanomodified polymers in stiff-elastic state [6].

The control of the form and flexibility of local zones of film made of stiff-elastic polymer allows manufacturing of materials for production of protective packaging elements with marking in form of "water-mark" which appears and disappears in process of highly elastic strain. The object of research consists in formation conditions, structure and properties of interval materials with reversible changeable transparency. In the theoretical part of this work were used the morphology presentations of polyolefine crystal structure and its effect on physical properties of the films manufactured by various methods expanded in classical monographs of known authors and in present-day reviews [7,8] .

2. THE RESEARCH SUBJECTS AND METHODS

The subject of inquiry are the films made of melt of isotactic polypropylene of XXX type by slot extrusion method by accelerated fivefold jet-stretching with cooling on a temperature-controlled steel cylinder by a patented technology of production of work materials for microcellular membranes [9]. The investigated pultruded films had strongly pronounced stiff-elastic properties and birefringent ability, insignificant opacity corresponding with transmission density of 0,01-0,05.

At the repeated straining of films lengthways, the preferred orientation results in effect of thixotrophic softening, typical for cross-linked elastomer [10] as well as in effect of reversible change of transparency [3]. The reversible change of transparency of stiff-elastic polypropylene films could be strictly localized on one narrow part of a material sample or in turn (periodically) on several narrow alternate areas. The film with such a structure is called an interval film [11] and can be made of nanomodified polymer by local thermal processing under pressure.

The interval thermal processing is a technological basis of the developed method of marking of polymer packaging and allows modification of local nanostructure of films made of amorphous-crystalline polymer which mechanism is not adequately explored. We have made an attempt of physical simulation of conditions and of experimental investigation of change processes of films crystalline structure by thermalphysic and mechano-optical methods.

The most applicable for manufacturing of packaging of consumables and mass printed products is amorphous-crystalline polyolefine: polypropylene and polyethylene.

The study of thermalphysic properties of stiff-elastic polypropylene was realized on a differential scanning calorimeter DSC 204 Phoenix/firm NETZSCH.

At the choice of program of temperature tests the heating-cooling interval is prescribed usually on the basis of $T_{пл} \pm 30^{O}C$. As the investigated sample of polypropylene film was manufactured under the conditions far from being in equilibrium, and in addition it was treated at a high heating speed; it was decided to expand the temperature span of experiment. The heating and the cooling were realized at the temperatures from $50^{O}C$ to $220^{O}C$ at an expected fusion temperature of polypropylene of $165^{O}C$. The tests of 10 samples were realized under the equal conditions by sequential increasing the maximum heating temperature with thermostating of samples and cooling them at a constant speed of 10 K/min. At each point of change of cooling/heating segment the temperature isotherm was set for 10 minutes.

3. THE RESULTS AND THEIR DISCUSSION

The differential scanning calorimetry heating curves (DSC curves) of an original unmodified sample of stiff-elastic polypropylene are shown on the figure 1. With a green line (curve 1) is marked out the first fusion of polymer in a DSC mesh; with a blue one (curve 2) – the repeated fusion. By the first fusion of stiff-elastic polypropylene is being broken down the non-equilibrium structure, which meets its stressedly-deformed state, and was formed while material manufacturing. Therefore the curves of the first fusion of the sample are

imaging its technological background; the curves of the second fusion represent an equilibrium state and properties of polymer, i.e. polypropylene of a certain type of which this film was made. The crystallization of polypropylene in the thermostatically controlled and repeated fused samples is realized in a DSC mesh off-site of processing equipment, under the conditions closer to equilibrium, i.e. under the "free" conditions.

As evident from these curves (fig. 1), the DSC curve has a flow form, and the crystallinity grade defined on the fusion peak area is considerably lower. The original stiff-elastic polypropylene sample is fused in the temperature range from 120ºC to 175ºC. The heat maximum, by heating is the mean fusion temperature of polypropylene for the first fusion is 168,9ºC, and for the repeated fusion - 167ºC. At the precision of temperature measurements of ±0.1^{O}C, taken by a device, is the temperature difference of 1,9ºC an established fact and tell the difference between the crystalline forms resulting by cooling of polypropylene in a DSC mesh and the crystalline forms of original film.

The crystallinity grade of a source material - defined in the NETZCH Proteus program as a relation of the fusion enthalpy for each case to the fusion enthalpy of a perfect crystal of polypropylene – equals to 5 percent; and for the repeated fusion - to 60 percent. The essential decrease of the crystallinity grade is caused by various conditions of crystallization of high-molecular polypropylene and by a great difference between the "age" of crystals in original film and in the sample, preaged by heat cycling in a DSC mesh.

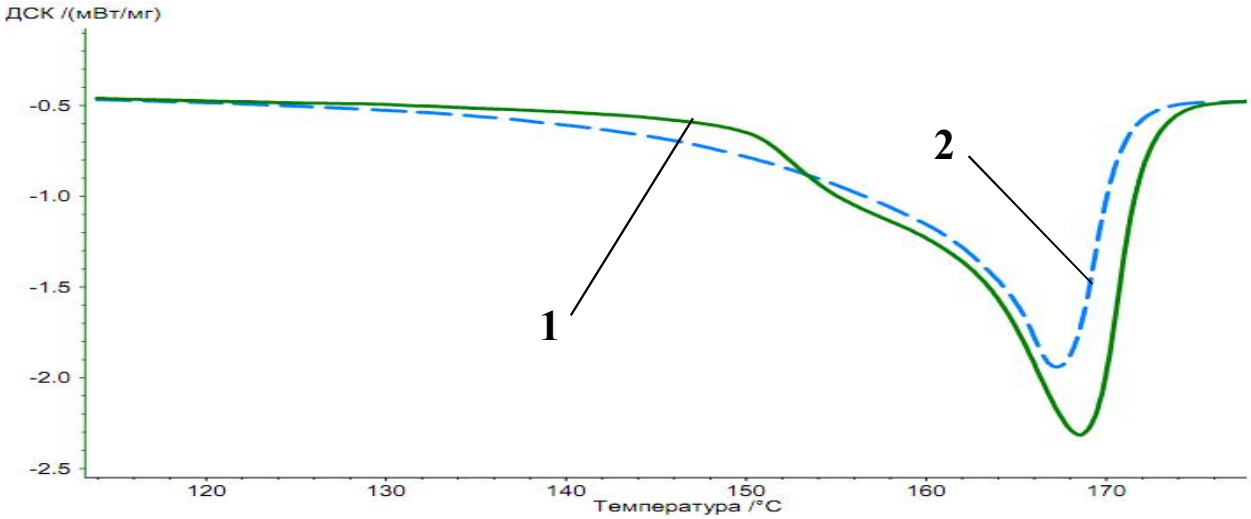


Fig.1. The DSC curve for an original unmodified stiff-elastic polypropylene sample.

The green curve (1) is the first fusion, the blue curve (2) – the second fusion.

The curve of a repeated fusion shows the properties of polymer of which the film was made, i.e. polypropylene of the given type. For the unmodified and the various modified samples the curves of the repeated fusion are analogous and are only of methodical interest as a method of additional confirmation of reproducibility of serial experiment conditions.

In this work is suggested and investigated the thermal modification of stiff-elastic polypropylene film by which the original crystalline structure of polymer undergoes some changes making for the subsequent mechano-optical effects (fig. 2), assumed as a basis for the water-mark conception on a polymer film printing material [6].

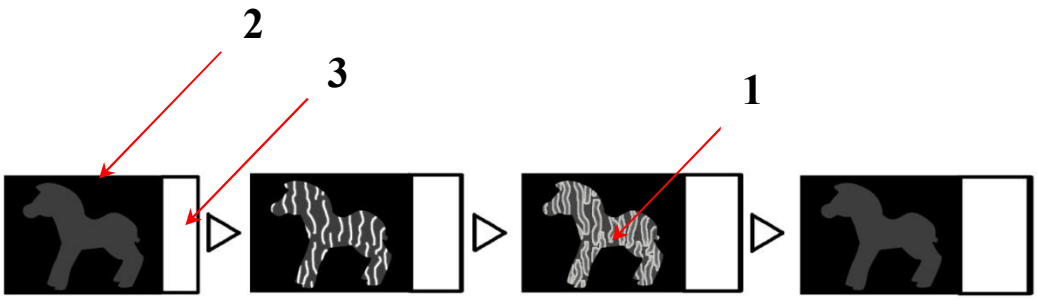


Fig.2. The mechano-optical showing up and disappearance effect s of "zebra" ornament (1) in a figure cut of a multilayer label tag (2) by tension of the tape made of modified stiff-elastic polypropylene (3) up to the various deformation rates.

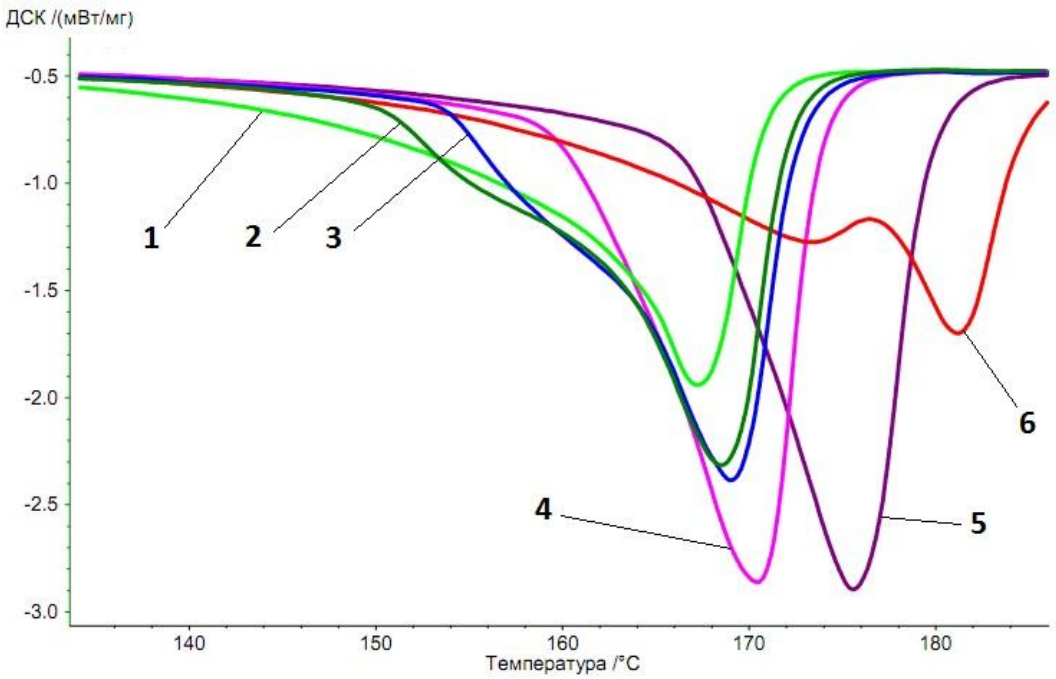


Fig.3. The DSC curves of the first fusion of original and modified samples of stiff-elastic polypropylene: the original sample -**1**; samples, heated to the temperatures:

150 ºC - **2**, 155 ºC - **3**, 160 ºC - **4**, 165 ºC - **5**, 220 ºC - **6**

For imitation of thermal modification of film and for definition of its effect on the crystal structure and the parameters of thermophysical properties of polymer were realized: the heat penetration of stiff-elastic polypropylene samples in a mesh of differential scanning calorimeter to the temperatures of 150, 155, 160 and 165^{O}C, the postheating stage at the given temperature for 10 minutes and the subsequent cooling at the speed of

10 K/minute. After cooling of warm samples to the indoor temperature was realized their full fusion standard testing. The received curves were compared with the curves of an original sample, i.e. a cold sample.
As a result of the tests were received the DSC curves in the temperature range of 21-220^{O}C for each sample with two fusion and crystallization cycles of polymer. The DSC curves of the first fusion of the sample to the full fusion temperature of polymer are of a special interest, as exactly this field is depending on the technological background of the sample, i.e. on the method and mode of its formation, the speed and the method of cooling (and accordingly its crystallization mode) as well as on the thermal processing, which causes by modification (in the second case) a considerable change of optical properties of the sample on the location area of a latent mark ("water-mark"). The received curves are shown on the figures 1 and 3.
On the figure 4 are shown the dependences of the key parameters of fusion process of the samples, defined as results of the tests. These diagrams of dependence of crystallinity grade, enthalpy and fusion temperature of polypropylene on the thermostating temperature at the conditions of heating and cooling at a constant speed.

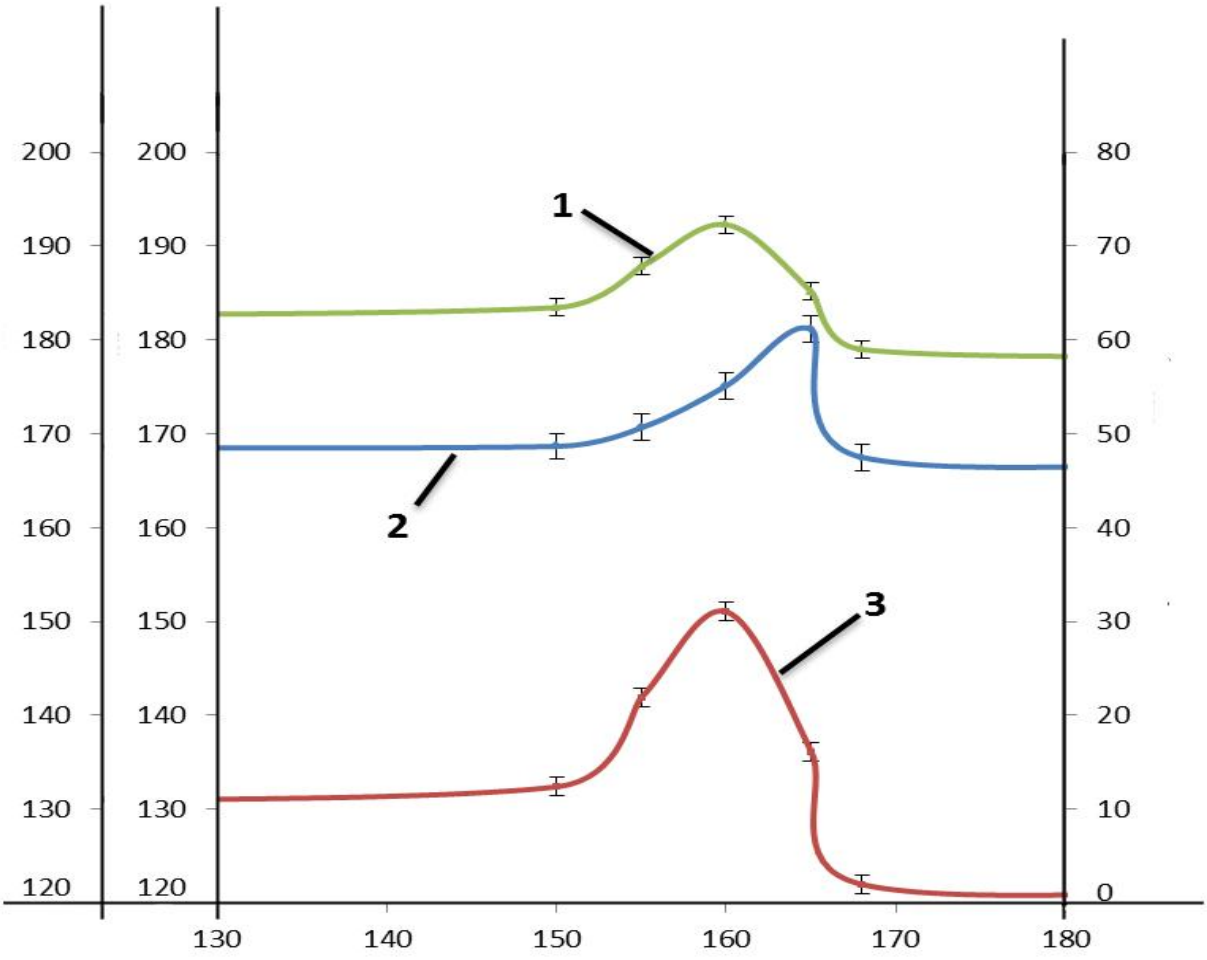


Fig. 4. The change of crystallinity grade α (curve 1), fusion temperature $T_{пл}$ (curve 2) and fusion enthalpy H (curve 3) of stiff-elastic polypropylene after its thermostating in a DSC mesh at various thermostating temperatures $T_т$.

The received diagrams demonstrate visually the presence of a temperature interval of a rapid precrystallization of polypropylene in stiff-elastic state. By heating to the temperatures of 150-168^{O}C at the speed of 10 K/min. the conditions for the ending of crystallization processes in stiff-elastic state are provided, that has an effect on the raise of crystallinity grade and fusion temperature. The heating to the temperature above 168^{O}C results in full fusion of a non-equilibrium crystalline structure of polymer and in formation of an equilibrium structure, corresponding with the thermostating conditions.

It is significant, that by the rise in temperature of preheating of polypropylene from 150^{O}C to 160^{O}C, the fusion temperature and crystallinity grade of polymer raise on 12,5 grades and 13 percent accordingly. The increase of crystallinity grade by the rise in temperature is caused obviously by the fact that at heating of film samples to the temperature of modification one part of crystals of polymer, which are probably fine and defective, are fused, and then under the conditions of thermostating and by cooling is realized the formation of crystalline particles of enlarged size with perfect structure, which have a higher fusion temperature than the fused crystals. The structure becomes less defective (there are less amorphous inclusions), what results in a substantial raise of crystallinity grade of polymer which increases from 62±1 to 72±1,5 percent.

The effect of increase of the average fusion temperature of stiff-elastic polypropylene in experiments with thermostating and repeated heating of film samples in a DSC mesh is probably a polymorphous transformation of polypropylene crystals. It is known [8, 12] that polymorphism phenomenon is typical for polypropylene. Polypropylene has 3 crystalline modifications with various fusion temperatures; the formation conditions of these modifications and the crystallographic description are represented in the known literature [12].

By manufacturing of stiff-elastic polypropylene films by extrusion of melt and with simultaneous stretch forming to 5-15 крат one part of polypropylene is crystallized in a beta (β) modification through a strong orientation of macromolecules. The most of crystals of stiff-elastic polypropylene are fused at the temperature of 140 – 160 ºC (figures 1 and 3). But at the thermostating at the temperature upwards of 150 degrees one part of beta-crystals is fused passing into a harder (high-melting) alpha modification, thereby raises the total average fusion temperature of polymer. In addition the lamels of an oriented structure in stiff-elastic polymer [13] could be result of the aftercrystallization of defective places of alpha crystals and amorphous phase between the lamels.

At the raise of temperature of film preconditioning before the fusion in a DSC mesh to the temperature of 165ºC and higher are reduced the heat quantitative characteristics. The fusion temperature and crystallinity grade change not symbatic, i.e. after the thermal processing the peak fusion temperature of the samples is shifted towards higher temperatures zone by 5-7 ºC in relation to the maximum fusion enthalpy. The level of both fusion characteristics after the thermal processing is 4 - 5 percent lower than the reference level. At the preprocessing of polymer at the temperature of 168ºC and higher the average fusion temperature, crystallinity grade and polymer fusion enthalpy are practically constant due to the new crystallization conditions.

The fact of constancy of average fusion temperature of polypropylene at the thermal processing in the temperature range higher than the fusion temperature of all crystalline formations confirms an assumption about the determining influence of the conditions and first of all of the cooling speed on the crystalline structure of films.

For the selection of optimal temperature for production of interval films with transparency gradient the stiff-elastic polypropylene sample was modified on the RDM TEST EQUIPMENT, a laboratory table simulator for sealing and thermal processing of polymer films at the constant programmable temperature and pressure.

The quality of produced samples of stiff-elastic polypropylene interval film with “zebra» water mark was visual estimated according to a seven-mark-scale.

On the table 1 is shown a matrix of values as an example of dependence of "zebra" image quality on the temperature and the pressure for the time of withstand pressure of 1 second.

Table 1. The Definition of optimum modification temperatures and pressing pressure of welding elements at the pressing time of 1 second

T, ^{O}C / P, кПа (psi)	120	130	140	150	160	170	180
208 (30)	2	3	4	4	5	4	6
276(40)	2	3	4	5	5	5	6
345(50)	2	4	5	5	5	5	6
414(60)	2	4	5	5	5	5	6
483(70)	3	4	5	5	5	6	6

On the basis of analysis of the whole of received data array including the results of thermal processing of samples within 0,1-1 second, at the pressure from 210 to 480 кПа and at the temperatures of 120-175^{O}C it was ascertained that the best samples were produced at following conditions:

1) T = 140^{O}C, t = 2 c, P = 414 кПа (60 psi);
2) T = 160 ^{O}C, t = 1c, P = 414 кПа (60 psi)
3) T = 170 ^{O}C, t = 1c, P = 345 кПа (50 psi)
4) T = 150 ^{O}C, t = 1c, P = 483 кПа (70 psi)

For the further investigation of stability of interval films and mechano-optical tests the sample number 4 was selected, as on this sample the modified interval in the form of a strip on "zebra" ornament had the most sharply defined frames, did not disappear after repeated extension, and retained its visual characteristics within 6 weeks.

4. THE CONCLUSION

In this work was experimentally proved the possibility of control of a repeatedly reversible change effect of stiff-elastic polypropylene film transparency. The conditions of manufacturing of interval films with a changeable transparency of optimum quality by a short-term local thermal processing at the temperature of 140-170^{O}C, at the pressure of 345-483 кПа are defined. There are investigated the possible mechanisms of rearrangement of crystal structure of polypropylene during the production of interval films of stiff-elastic polypropylene; as well as the definition technique, quantitative characteristics and qualitative description of a repeatedly reversible change effect of transparency in polymer film materials meant for the manufacturing of protective elements of packing were offered.

ACKNOWLEDGEMENTS:

The present work is supported by Ministry of education and Science RF. Contract on 10.10.2011 г. №16.513.12.3022

REFERENCES

1. Efremov N.F. (2009), The Package and its production, part1, Production of container of polymer films and sheets, Moscow, MSUPA, 2009, p. 341.
2. Babljuk E.B., Kondratov A.P. (2011) The application for the invention of Russian Federation No. 2010108169, MPK B65 D 81/00, Method of counterfeit protection of printed production, 10.09.2011, p. 18
3. Kondratov A.P. (RU), Babljuk E.Б (RU) (2010), Patent of Russian Federation No. 97844 МПК G09F, The multilayered protective label with a planar stress concentrator; applicant and patent holder: MSUPA, the application No. 2010120834 of 25.05.2010, published 20.09.2010, Bulletin No. 26 of 20.09.10, p 6.
4. Kondratov A.P. (RU), Benda A.F. (RU), Erofeeva A.V. (RU) (2010), Patent of Russian Federation No. 97843 МПК G09F3/00, The information protective label; applicant and patent holder: MSUPA, the application No. 136307 of 13.03.2009, published 03.04.2010, Bulletin No. 26 of 20.09.10, p 10.
5. Kondratov A.P. (RU), Babljuk E.Б (RU) Erofeeva A.V. (RU), Shulina T.M. (RU) (2010), Patent of Russian Federation No. 98987 МПК G09F. Film packing, counterfeit protected, applicant and patent holder: MSUPA, the application No. 2010108059 of 04.03.2010, published 10.11.2010, Bulletin No. 31 of 10.11.10, p. 25.
6. Kondratov A.P., M. A.Д, Hursa V. I, (2010), Polyolefine films with "water-mark" for the protected printing, News of High Schools, Problems of Polygraphy and Publishing, No. 4, 2010, p. 64-50.
7. Edited by Pilipovsky and I.K. Yartsev, Polypropylene, translation from Slovak by V.A. Egorov, (1967), "Chemistry", 1967, 316 p.
8. Frank van der Burgt (2002), Crystallization of isotactic polypropylene: the influence of stereo-defects, Technische Universität Eindhoven, 2002, 112 p.
9. A.I.Mzhelsky, S.V.Zarenin (1993), The method of production of microporous polypropylene films, Patent SU 1809810, published 15.04.93.
10. A.P.Kondratov, Patrikeev-Mallins Effekt (2010) at the deformation of latex rubber products //Caoutchouc and Rubber, № 1, 2010, p. 21-25.
11. A.P.Kondratov (2010), The gradient and interval heat-shrinkage materials for counterfeit protection of printed products//News of High Schools. Problems of Polygraphy and Publishing, No. 4, 2010, p. 57-65.
12. A.A.Tager, edited by A.A.Askadsky (2007), Physical chemistry of polymers, the 4th edition, revised and complemented, Moscow, The Scientific World, 2007, 576 p.
13. Karpov E.A., Lavrentev V. K, Rozova E.J., Eljashevich G. K. (1995) The change of structure and mechanical properties of stiff-elastic samples of polyethylene by the annealing.//High-molecular compound, 37A, No. 12, 1995. p. 2035-2042