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INTERVAL SHRINKABLE MATERIALS WITH "SHAPE MEMORY" FOR THE COUNTERFEIT PROTECTION OF PRINTED PRODUCTS AND PACKAGING

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Abstract

The Intervals (zones) with different shrinkage are formed in thermoplastic polymer films by the local modification of their structure on the defined material zones; they are specific "watermarks" which are invisible under the layer of printing ink. By printing of the information marks, which are consisting of thin lines, on the film is manufactured a product (brand mark, label etc.); the authenticity of this product can be tested by temperature increase up to the defined grade, which provides a heterogeneous shrinkage of polymer film. The heating of interval shrinkable film at strongly controlled conditions is a basis for the showing up of latent and tactile marks. The dilatometric and calorimetric studies allow the estimating of the optimal value of shrinkage and effect of "shape memory" on various interval films.

Key words: *printing industry, packaging, tag, label, "shape memory", shrinkable films, differential scanning calorimetry (DSC)*

1. INTRODUCTION

There is an objective necessity for counterfeit control of printing products in Europe and Russia now. The current acuteness of this problem is determinated in many respects by the development and a wide distribution of printing equipment. The firms and state enterprises, which are producing unique products and securities, are continuously improving the process of production and the methods of counterfeit protection. The range of protection of printing products is determined by three components, there are the complexity of processes, the limited access to materials and equipment, the novelty and inaccessibility of actual methods. For the counterfeit protection of commodities brands of mass consumption goods, e.g. cosmetics of known firms or ecological pure products for baby food, are developed composite multilayer labels made of bright, shiny, flickering, flexible, textured etc. self-adhesive materials with a temporary (weak and multiple) fixing [1].

The multilayer, composite and self-adhesive labels have an effect on the buyers as a magnet attracting attention to the new or known goods of a known brands producer. The attraction is based on the possibility of detection of a discount, a prize or additional latent information about the goods. The "unstick and read" labels give the manufacturers an opportunity to use it for the purposes of widest advertising and marketing. The counterfeit of such labels is not difficult and could be realized easily and quickly on the copying or printing equipment. One of the efficient methods of counterfeit reaction is the using of special printing materials which could be authenticated by customer or representative of brand producer.

We proposed [2, 3] using of shrinkable polymer film materials with "shape memory" for counterfeit protection. The application variants of such materials for counterfeit control of printing products are

shown below. There are multilayer labels (fig. 1), unstuck labels on the packaging of product, which could be warmed up in its container (fig. 2), and labels for tea bags (fig. 3).

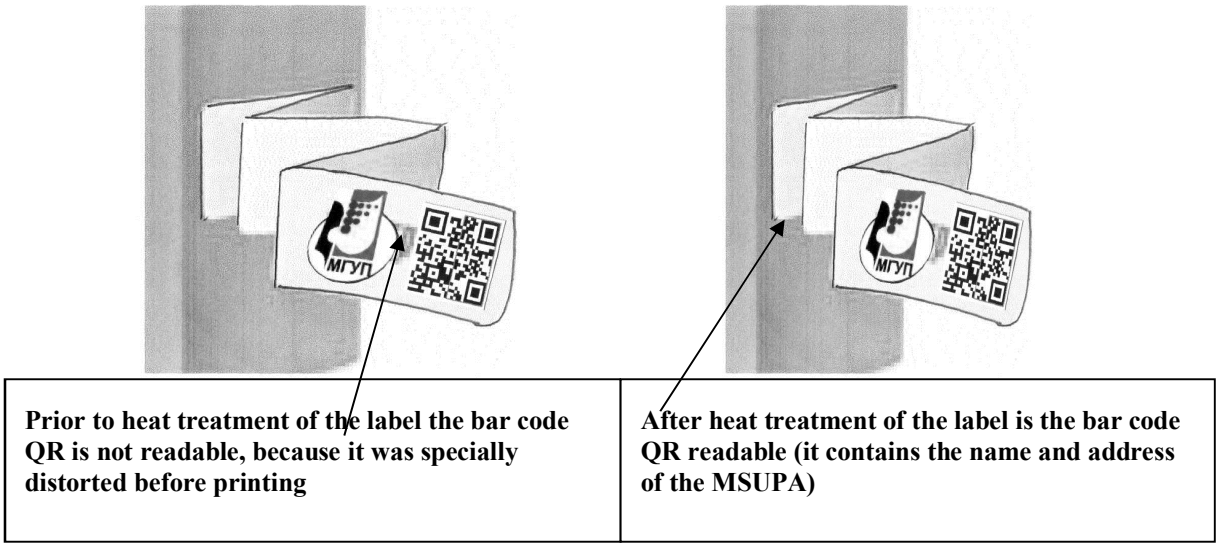


Figure 1. The scheme of a complex book-shaped label made of interval heat shrinkable film with the MSUPA logo and protected bar code

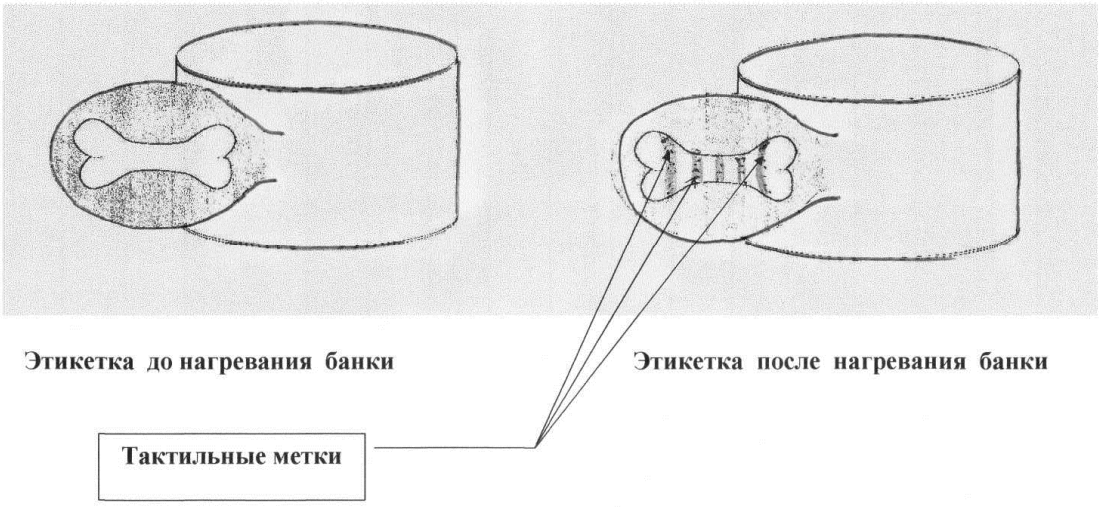


Figure 2. The scheme of an unstuck label with tactile marks appearing at heating in oven, water, etc.

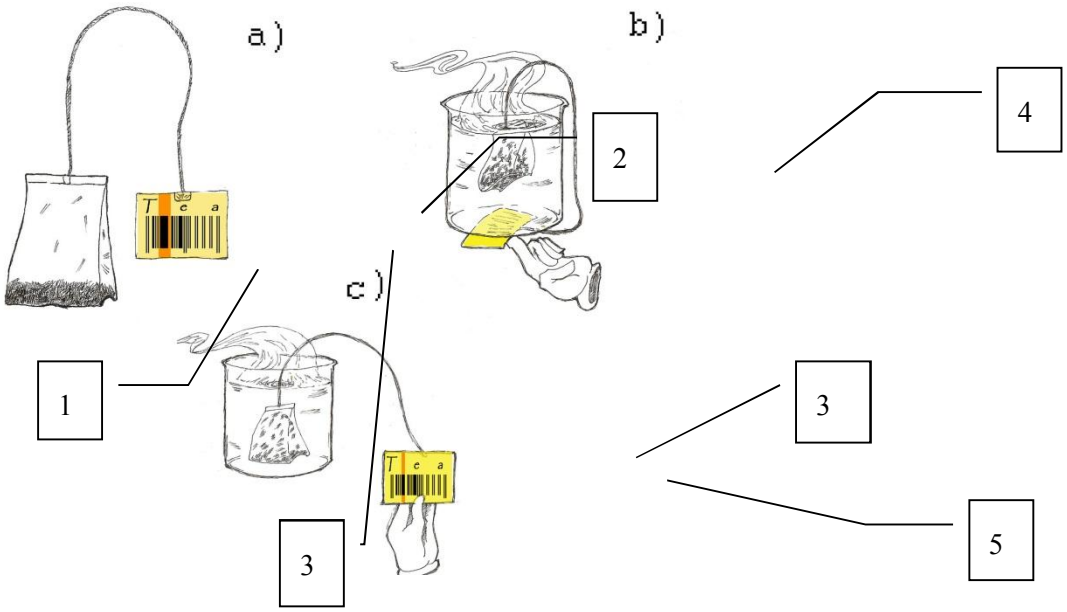


Figure 3. The scheme of a tea bag (1) with a protective label (2) made from an interval shrinkable material with "shape memory". A tactile label (3), a cup (4), a bar code (5), which appears and are readable by scanner only after heating of the label

2. THE EXPERIMENTAL PART

For the realization of dilatometric and calorimetric studies and designing of protective details of packaging, multilayer labels and tags made of the new interval shrinkable polymer films there were used thermoplastic polymers, such as polyvinylchloride (PVC) in the form of shrinkable film and polyethylene (PE) in the form of film, produced by extrusion with tube ballooning. The narrow zones with minimum shrinkage were formed in anisotropic thermoshrinkable PVC films by the local heat treatment under pressure in a free state and with fixed sizes. The zones with maximum shrinkage in isotropic polyethylene films were received by a local deformation of the narrow zones of ribbon samples on 300÷500 percent at 20ºC. On the samples of interval films of both types was applied by screening a millimetric coordinate grid for realization of dilatometric measurements in film deformation and shrinkage processes. The "shape memory" effect on the samples of interval film materials made of PVC and PE was showing up at the heating temperature from 60ºC to 100ºC.

At calorimetric studies of interval films with "shape memory" were cut out the microdisks of these samples for placing in a crucible of differential scanning calorimeter (DSC). There were used the aluminium crucibles 5 mm in diameter with holes; and the calorimeter with a software for diagrammes processing on a PC - DSC 204 Phoenix, firm NETZSCH (Germany). For realization of a controlled shrinkage of interval films in various and strictly reproducible conditions was used a standard technique of shrinkage properties assessment (GOST 25951-83), a specially developed mesh [4] and a pack laminator "Prolamic HR 330 D", firm ProfiOffice (Germany).

3. THE RESULTS OF THE THEORETICAL AND EXPERIMENTAL STUDIES AND THEIR DISCUSSION

The degree of local structure heterogeneity of polymers and heterogeneity of local film shrinkage are significant for printing industry, especially for production of protected elements of packaging, should

be commensurable with the cross sizes of the line elements of printed image, e. g. bar code; and have an average size not less than one millimetre. The film zones with a local shrinkage on the protective packaging elements made of polymer films, different from that one on the other part of material, are repeated as a rule at a distance of several millimetres. On the figure 4 is shown as an example a fragment of PVC film with a latent "water mark", intended for manufacturing of counterfeit protected flexible packing. The interval film takes this form after heat treatment in hot water. The photo is taken by transmitted light microfilming through the microscope objective with low magnification. In the given example (fig. 4) the modification process represents a local heat treatment of a narrow zone (of 1,5-2 mm) of shrinkable film during 0,5÷2 seconds to the temperature of 85÷100ºC with a subsequent retention interval under pressure up to the cooling to the temperature below polymer vitrification temperature.

On the interval shrinkable film sample was applied a layer of an opaque light ink by flexographic proof press “Flexiproof 100 RK”, and after that by screen printing was formed an image consisting of parallel dark strips. The "water-mark" is invisible on the print.

After heat treatment of a printed sample, e.g. using a blow dry air stream heated to 100 ± 15 degrees centigrade, a pack laminator or by its sinking in hot water on the film surface appears a cross-shaped water-mark", hidden in polymer structure; this mark is clearly discernible with naked eye, and can be tactile sensed (to the touch) by blind or purblind persons.

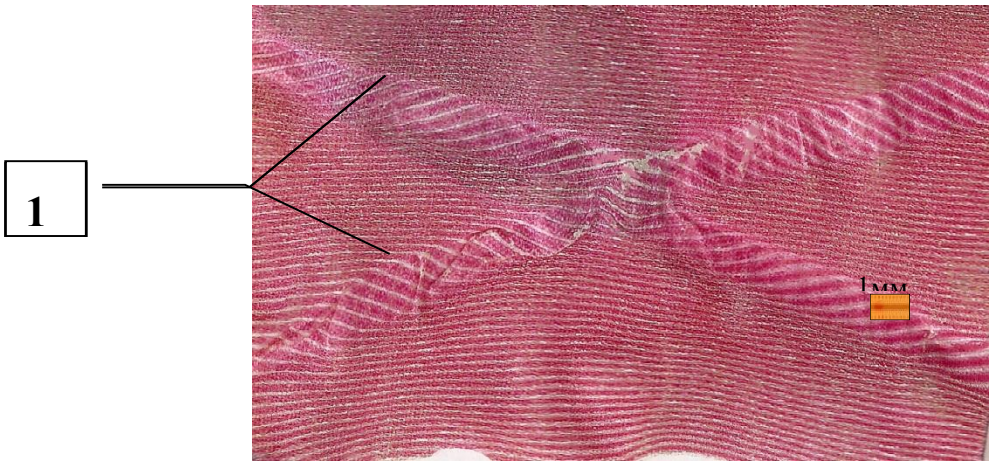


Figure 4. : The photomicrography of sample sections of printed heat shrinkable polyvinylchloride film with a "water-mark", identified by heat treatment. Tactile mark (1).

The efficiency of visualization and the possibility of tactile identification of a “water-mark" on an interval film depends first of all on geometrical factors and on ratio of local shrinkage magnitudes of polymer on the modified and not modified zones.

We investigated the dependences of films shrinkage range in the modified zone ("a watermark" zone) and in abutting zones on the modification temperature in the range of 70÷96 degrees centigrade at the time of local heat treatment under pressure of 5÷7 seconds. Under these conditions depending on pressure and fixing of the sample sizes in the thermoshrinkable film are taking place several interconnected relaxation processes: shrinkage (reduction of not fixed sizes of a film sample, drop of internal stress at the heating and increase of internal stress in the heated zone after cooling).

The last process of internal stress increase at the film cooling after heating with a fixed length is abnomalous. The drop of stress in the thermoshrinkable polyvinylchloride film sample at its cooling after heating to the temperature higher than the vitrification temperature does not correspond to the known concepts of relaxation mechanisms [5,6].

This unconventional "shape memory" effect is worthy of special studying. On the figure 5 is shown a change of stress in the thermoshrinkable polyvinylchloride film sample in the heating by hot air with a subsequent cooling in the stationary tensometer clips.

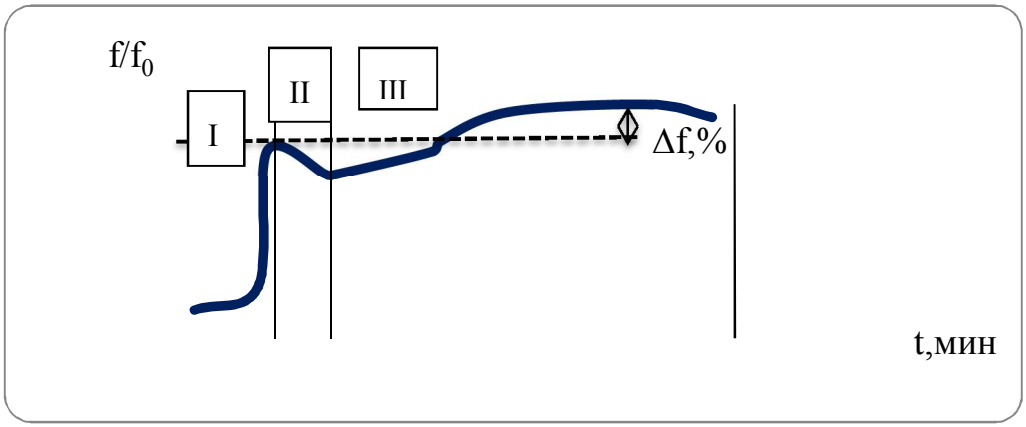


Figure 5. The change of stress in the shrinkable PVC film at heating and cooling in the stationary tensometer clips.

The tensometric curve has a strange form and can be divided into some characteristic parts. The first part is the curve of a rapid increase of stress in a sample with a fixed length at heating to the PVC vitrification temperature (I). The achieved level of shrinkage stress we recognize as one. The relaxation (II) of stress begins in thermostating process of the sample at the temperature above the vitrification temperature (80ºC). At this stage the stress drops is going down to 0.8, i.e. by 20 percent. The side counteraction of thermoshrinkable film is to be observed. The time of stress relaxation to the level 0,8 is in order of 1 minute. The stress relaxation effect at heating is well corresponded to the theoretical concepts of the stress relaxation mechanism in stressedly-deformed polymer [6]. At the sample cooling, at the stage (III) is to be observed an anomalous increase of internal stress in the film to the level of 1.2. This stress increase by 20 percent as against the original one is not a maximum possible one. If the same sample is heated a few times (fig. 6), the regress processes described above and the subsequent stress icrease are repeated in the same order but with a lower speed. The characteristic time of relaxation on the regress areas reflects in a quantitative sense the speed of bipolar stress change in the film (table 1). The total stress increase in thermoshrinkable film samples at cyclic heating and cooling was 80 percent.

Table 1. The **s**peed of relaxation processes in the PVC thermoshrinkable films with a fixed length at the heat cycling

Cycle No.	Overstress (Δf), %	Relaxation time ($\tau_{рел}$), minute
1	28	8
2	32	21
3	12	56
4	8	–

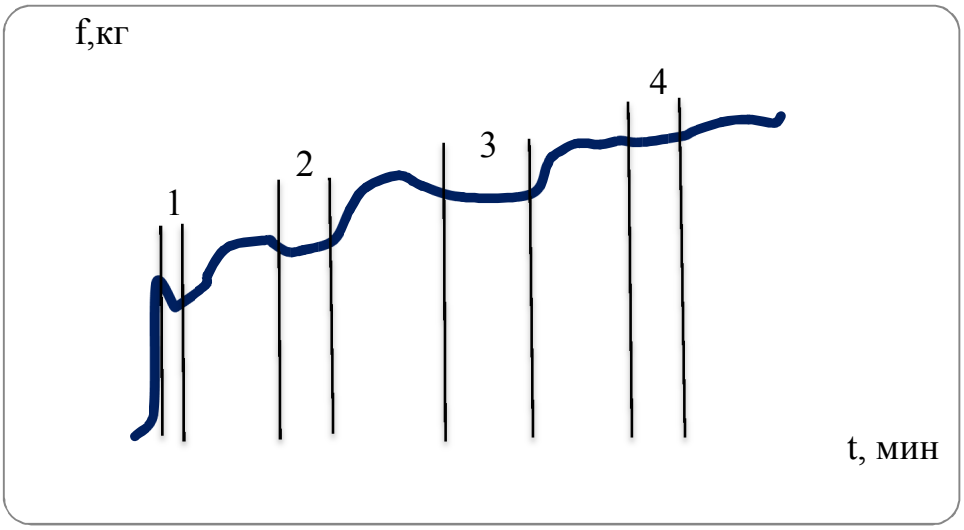


Figure 6. The bipolar stress relaxation in a thermoshrinkable film at the heat cycling.

For studying of the mechanism of this phenomenon there were realized the dilatometric and calorimetric studies of original thermoshrinkable polyvinylchloride films and the samples made of these films, heated under pressure. The film-loading pressure at the local heat treatment was realized by pressing between the flat metal plates which provided the fixing of film sizes at the heating due to the friction force hindering the film slipping lengthwise the plates at the shrinkage behavior.

For the shrinkage measuring at the heating it was applied by screen printing a coordinate grid on the samples of original thermoshrinkable film with homogeneous shrinkage along the full length of the interval film. The distorted grid after shrinkage was studied under a microscope. The local shrinkage of the modified intervals is shown in various rates depending on the methods of its evaluation and on the used device. We have used three techniques of quantitative assessment of shrinkable polymer materials deformation, there are the heating in a water bath, the heating in a dry-air thermostat (in accordance with GOST No. 25951-83) and the heating in a laminator between two sheets of heat-resistant polymer with a release coating [4]. The received results were tabulated and shown on the figure 7.

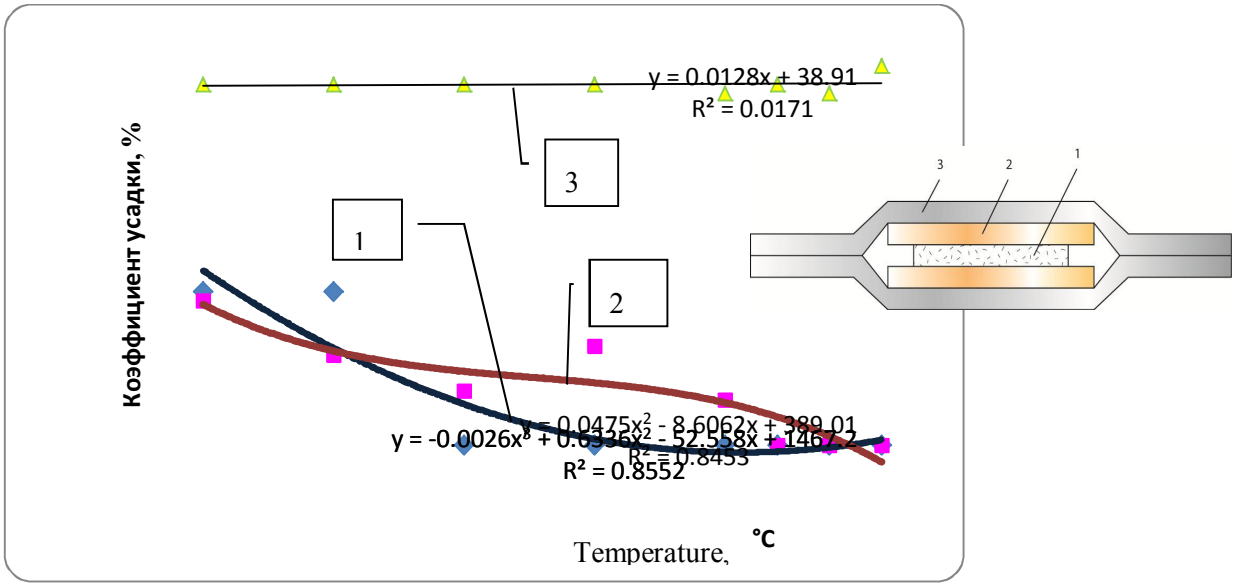


Figure 7. The local shrinkage of the modified intervals (1, 2) and of the not modified shrinkable PVC film (3) at the heating of samples in a free state in water (1,3), in laminator [4] (2,3) and in dry-air thermostat in accordance with GOST 25951-83 (3).

There is evident from the received results of measurements, that the application of a special cell for the rapid heat treatment in laminator [4] as a technical appearance medium of interval film local shrinkage heterogeneity gives a practice-important advantage. Already at 80°C the reduction of linear sizes of the polyvinylchloride film zones, subject to heat modification, is equal to 0; and the local shrinkage distinction on the neighbour film zones run up to the maximum values. The shrinkage gradient on zones borders of polyvinylchloride film, subject to modification, makes 0,3÷0,8 mm^{-1} and depends on the type of polymer material, as well as on the method of local modification and the preferred orientation value of macromolecules in original polymer material.

The modification of thermoshrinkable interval film zones by cold stretching gives a rather smaller "shape memory" effect but it allows receiving a shrinkage gradient of 0,45÷0,6 mm^{-1} in a transitive zone of 1÷1,25 mm in length.

The absolute value and the local shrinkage gradient of interval polymer films of both types, subject to oriented stretching by production of thermoshrinkable materials and formed in the orientation process by deformation (under normal conditions) can be quantitatively assessed by several physicomechanical and thermophysical methods. We have used the microscopy, macrophotography, dilatometric and calorimetric analysis (DSC).

Table 2. The deformation of intervals reduction with a minimum shrinkage in interval films of various types, there are the modified polyvinylchloride film and the polyethylene film.

Processing temperature of the interval,°C			Minimum shrinkage of the interval film, %		Shrinkage gradient, mm^{-1}	
No.	$t_{верх}$, °C	$t_{нижн}$, °C	laminator	water (100°C)	laminator	water
Shrinkable polyvinylchloride «Eurofilm» (maximum shrinkage: 40 percent)						
1	70	70	17	16	0,43	0,20
2	75	75	17	10	0,43	0,25
3	80	80	0	6	0,33	0,28
4	85	85	0	11	0,33	0,24
5	90	90	0	5	0,33	0,29
6	92	92	0	0	0,33	0,33
7	94	94	0	0	0,43	0,33
8	96	96	0	0	0,48	0,40
Shrinkable polyvinylchloride «Don-Polymer» (maximum shrinkage: 50 percent)						
9	80	80*	-	0	-	0,23
10	110	110**	-	0	-	0,80
11	112	112***	-	0	-	0,89
Low-density polyethylene (maximum shrinkage: 63 percent)						
12	22	22****	-	0,6	-	0,49
13	22	22****	-	0,4	-	0,50

*) transition zone length 1,25 mm; **) transition zone length 0,63 mm

) transition zone length 0,63 mm; *) transition zone length 1,25 mm

The shrinkage of interval films proceeds spontaneously at heating under the influence of internal stress [5], due to the energy absorbed by polymer in film formation process.

By the example of polyvinylchloride, polystyrene and its copolymers with methacrylic acid it is shown [6] that the polymer material, deformed in glassy state by 30÷40 percent, reserves about 5÷6 joule of internal energy per one gram of polymer. The influence of the forced-elastic deformation on the thermophysic constants of a glassy polymer is shown as follows. The DSC diagramme of a deformed polymer contains a wide exothermic peak below the vitrification temperature, and the DSC diagramme of not deformed polymer contains only an endothermic peak in the field of its vitrification temperature. In low- annealing process the exothermic is gradually displaced to the area of high temperatures and decreases; and thereupon disappears completely after a long heat treatment in free condition. The endothermic peak grows in the annealing process on the contrary. These experimentally verified facts show that the physical deterioration process and internal stress relaxation process in structure of deformed glassy polymer are accompanied by thermal effects of the opposite signs [6].

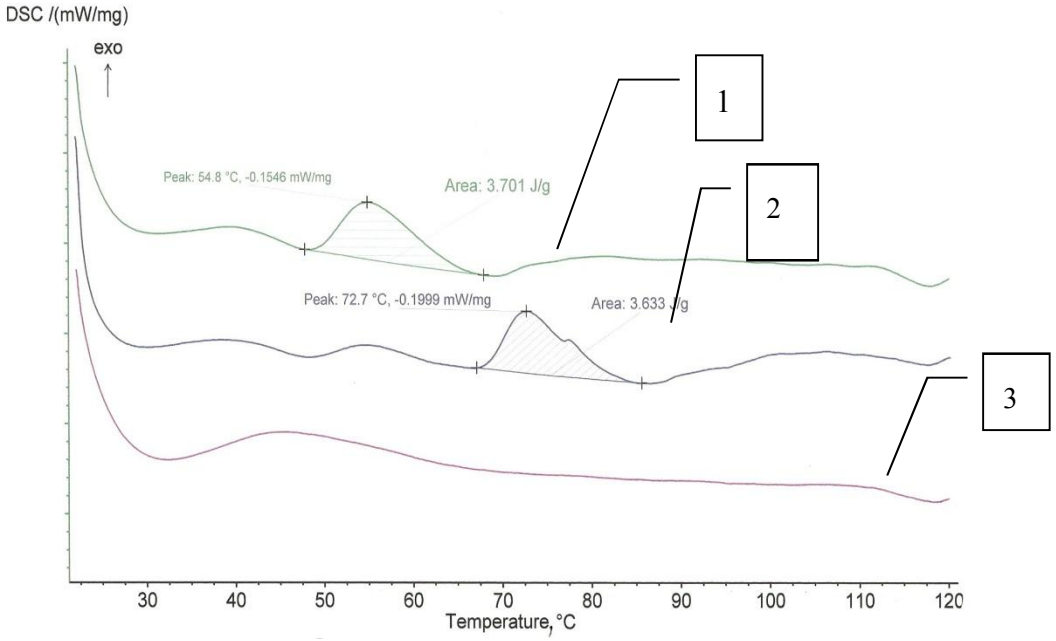


Figure 8. The DSC curves of polyvinylchloride film samples with characteristic exothermic peaks. The original film sample, unprocessed (1). The sample, thermal processed under the pressure of 70 psi at 90ºC during 90 seconds (2). The sample at the repeated heating in the crucible of the DSC calorimeter (3).

The DSC diagrammes of the first heating and the repeated heatings of the thermoshrinkable polymer material samples differ in quality (fig. 8).

On the studied samples it is established that the diagramme of the first heating of thermoshrinkable polyvinylchloride films, and the films, heated in boiling water for short-time (for 5 seconds), has an exothermic peak corresponding to the temperature of the oriented stretching during the production. If. If the film is modified by heat treatment at 70-80ºC under the pressure of 70 psi within 90 seconds the exothermal peak is displaced to the polyvinylchloride vitrification temperature area. The amount of energy liberated by the shrinkage makes 3,6÷3,7 J./g; and does not change practically in the modification process of thermoshrinkable polyvinylchloride by local heat treatment under pressure i.e. the normal pressure, due to the friction on the contacting surfaces, prevents from the film shrinkage at the heat treatment. In the places of local heat treatment under pressure remains the previous level of internal stress; and the exothermic effect is shown in the same rates at the subsequent heating, but at the higher temperatures.

In many experimental studies of glassy polymers by the deformation calorimetry method it is shown [7-12] that the plastic deformation of polymer glasses differs in principle from the corresponding process which takes place in low-molecular solid bodies. The considerable part of deformation work at the initial stage of "cold" stretching or linear pressing is accumulated by a polymer body and is not be transformed into the heat [10], without an additional heating of deformed samples in a free condition. For the description of thermophysical effect features and mechano-structural behaviour of glassy polymers there were suggested some hypotheses stated in the monography [13]. The essence of these hypotheses consists in the analogy between the “forced-elastic deformation” and the “forced-

elastic relaxation". The application of conformable terms shows the commonality of the deformation mechanisms and the afterreduction of deformed polymer.

Our investigations show that a determinating factor is the physical condition of polymer, at which the processes of forced-elastic deformation and the forced-elastic relaxation are realized. The thermal effects accompanying the shrinkage have opposite signs, i.e. are exothermic or endothermic in a glassy and a hyperelastic state. In glassy polyvinylchloride the forced-elastic relaxation proceeds with an exothermic effect, and the similar process in elastic amorphous-crystalline polyethylene is accompanied by an endothermic effect (fig. 9).

The intensity of endothermic effects is rather lower.

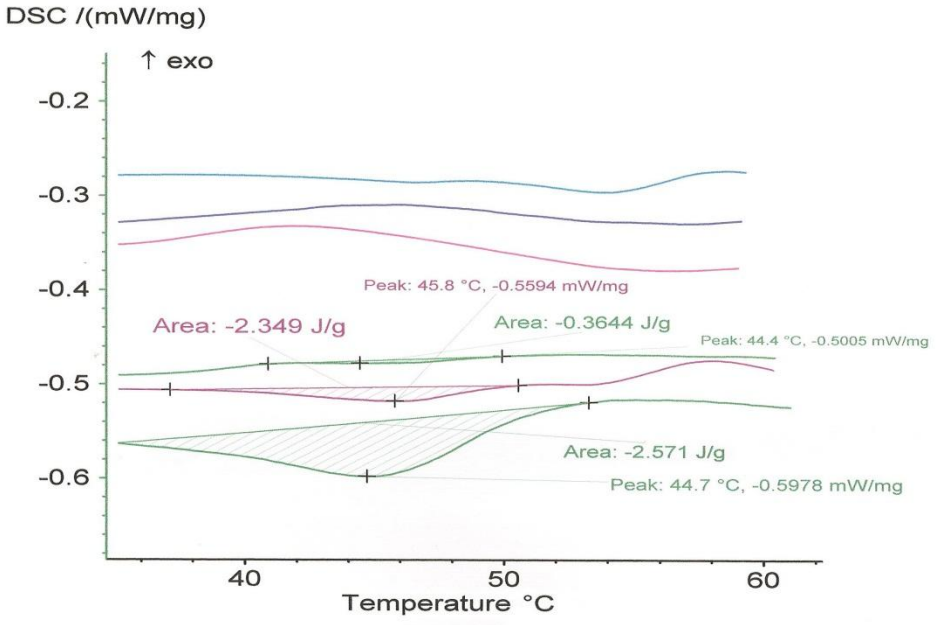


Figure 9. The DSC curves of polyethylene film samples with characteristic endothermic peaks

The size of thermal shrinkage effect of amorphous-crystalline polyethylene changes in the range of 0,3 - 2,5 J./g and depends on the conditions of forced-elastic deformation. The higher is the stress aapplied to the sample at stretching, the more resilience energy it reserves and the greater is the shrinkage. At the same time the dependence of the shrinkage on the stress and stretching size of film is not linear (fig. 10), and has intervals of minimum and maximum values of 150-200 percent.

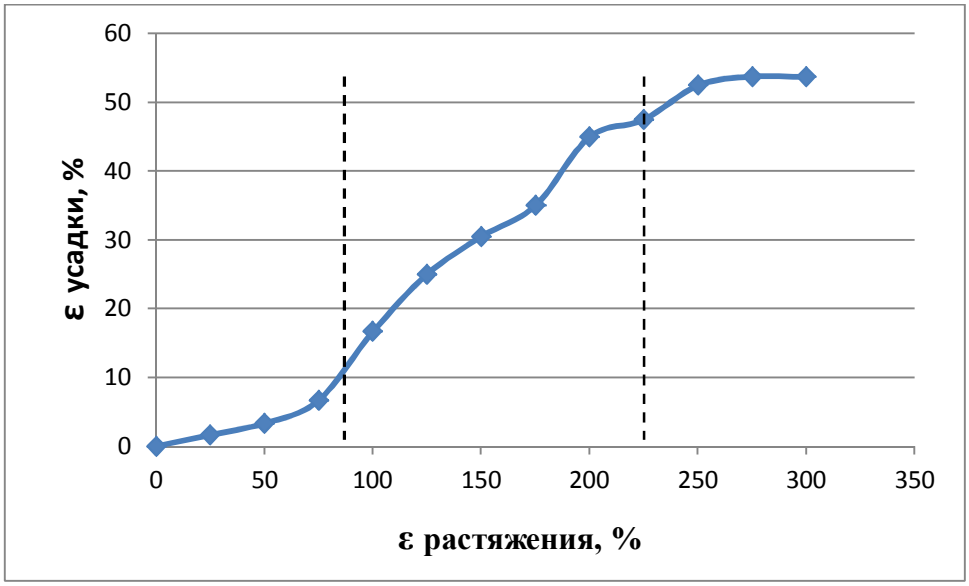


Figure 10. The dependence of polyethylene film shrinkage on the stretching degree.

Under the adiabatic conditions the deformed polyethylene film shrinkage is accompanied by the heat absorption and the growth of polymer macromolecule entropy in the disorientation (fig. 9).

As a result of low thermal conductivity of polyethylene and specific surface of the layered sample, placed in the DSC crucible, it is lawful to consider the shrinkage process to be adiabatic. Under the adiabatic conditions the jumping increase of macromolecular system entropy in consequence of the shrinkage is accompanied by temperature pulldown of the polymer film sample. The endotermic effect is the more; the higher is the level of internal stress in thermoshrinkable polyethylene.

4. THE CONCLUSION

The local structure change of thermoshrinkable polymer films under controlled conditions by using of "shape memory" effect allows manufacturing of a wide set of modified packing materials for original production and creating of a new technology of brands counterfeit protection of bulk commodities. The offered materials and the developed on their basis methods of material science for printed products counterfeit protection excel the similar technical solutions in usability of large-capacity polymers, high-performance equipment for thermoplastics processing into oriented or thermoshrinkable films with an insignificant design debugging, as well as in the applicability of high-speed printing (planar) technologies of data recording on roll-to-roll films.

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