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The process of tactile (relief) marking of thermo shrinkable membranes and labels

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Abstract. Authors propose a new method of information recording in the form of a relief on the surface of a membrane or film made of the thermo shrinkable polyvinyl chloride. The information is recorded with the help of printing equipment. The printing equipment should undergo partial modification to increase contact time of the film with liquid ink on a printing plate. The ink contains certain ingredients that quickly dissolve the film and reduce local internal compressive stresses in the contact zone. The paper represents the shape and size of the relief elements formed on a membrane made of the thermo shrinkable polyvinyl chloride using screen printing with the ink containing a solvent – tetrahydrofuran.

1. Introduction

Safety of a modern person living in an urbanized area with many power supply utilities, hazardous products and chemicals depends on how fast and certain these hazards can be identified. For quick identification of dangerous objects and communications, we use the following methods: light, color, smell, and sound. Tactile membranes and labels are much more rarely used. In some cases, there is no alternative to tactile information about the objects in contact with a person, and the joint use of vision and touch significantly increases safety and comfort of many household and industrial processes. For this reason, the European Union [1] standards provide for mandatory tactile marking of medicines. There is an obvious need for relief marking of such household products as sanitation, cosmetics, paints, food as well as assembly parts and hand tools [2-5]. Tactile marking allows ordinary consumers and people with reduced capabilities (blind or with impaired vision or attention) identify objects and control authenticity of consumer goods. Tactile identification makes it easy to operate cables and pipelines located in hard-to-reach and inadequately lighted areas.

Relief symbols of tactile marking can be created on objects and materials by various ways using existing technical means. For example, blind or hot stamping equipment is used for tactile (relief) marking of sheet polymer materials [6, 7]. Heat-resistant sheet and roll materials can be labeled with a relief using a printing equipment that implements all types of printing as well as using a 3D printer [8-14].

Traditional methods does not allow to print and create a relief on fusible and thermo shrinkable materials, widely used for manufacture of product labels and membranes, due to their low heat resistance. To mark the products made of thermo shrinkable materials, the authors propose an original method of local isometric heat treatment which allows to create relief images and informational signs in Braille without the use of paints and additional consumables [2, 8].

Tactile (relief) marking of thermo shrinkable materials is based on two main operations: the first is local heat treatment under isometric conditions at a certain temperature and holding time under pressure, the second is heating of the entire label or membrane on the utilities at a temperature exceeding the glass transition temperature of the polymer [15].

Geometric parameters of tactile (relief) marking on thermo shrinkable materials, membranes, couplings, etc. are determined by the size and anisotropy of material size reduction (shrinkage) during processing using the automatic equipment — a hot air stream or superheated water vapor applicator [16]. Thermostimulated size reduction of a thermo shrinkable material on containers, utilities, cables, tools, equipment levers, etc. with the appearance of tactile (relief) marking is determined by the relaxation rate of internal stresses in polymeric materials and the patterns of reduction (compression) of the thermo shrinkable films subjected to local isometric heat treatment in the area of tactile (relief) characters.

It is known [17] that the rate of relaxation processes occurring in thermo shrinkable films during heating depends on the ambient temperature and composition of the polymer film. The authors put forward a hypothesis about the possibility of relaxation processes acceleration in local areas of the thermo shrinkable film forming a relief when heated by preliminary short-term treatment using a liquid with high thermodynamic affinity to the polymer, i.e. good volatile solvent or plasticizer [6, 18].

The purpose of the paper is experimental verification of the hypothesis and substantiation of the possibility of tactile marking of thermo shrinkable membranes and labels by means of short-term liquid treatment using printing equipment.

2. Subjects and methods

To obtain the initial data necessary for development of the marking method, we used a thermo shrinkable film in the form of a sleeve (membrane) manufactured by Dongil Chemical company with the film thickness of 80 μ m and flat sleeve width (half-perimeter) of 55 mm. The minimum thermal shrinkage in boiling water is 60%. The start temperature of thermal shrinkage is 55 °C. Film composition: suspended polyvinyl chloride (92%), dioctyl phthalate (4%), calcium stearate, polyphenyl methylsiloxane – 3%, epoxidized soybean oil – 3%.

As solvent and plasticizer compatible with polyvinyl chloride, we used tetrahydrofuran (AR) in the form of solutions in distilled water and basic paint used to reduce the color intensity as a varnish of the HIGLOSS VINIL 35800-00 brand with tetrahydrofuran.

In order to physically simulate the process of short-term interaction of tetrahydrofuran (THF) aqueous solutions and the polyvinyl chloride film, we developed a technique for accurate registration of the contact time and size of the film samples (isometric mode of swelling and dissolution).

We put a sample of the thermo shrinkable polyvinyl chloride film in the form of a circle with the diameter of 110 mm into a heavy jar made of thick glass (figure 1a). The jar is closed by a sealing cover with a clamp (figure 1b) and turned over (figure 1c) for the period of 1 to 10 minutes. Since the heat capacity of the liquid in the jar is quite high, this ensures a constant temperature during the polymer swelling (from 1 to 10 minutes). After each test, we place the jar with the solution to the tank of the water thermostat (bath) with heated water to maintain temperature of the tetrahydrofuran solution.

After the predetermined time of exposure to the tetrahydrofuran aqueous solution on one surface of the polyvinyl chloride film at a constant temperature, the heavy jar is turned over to its original position. After the cover is removed, the studied film sample is taken out of the jar and immersed in a container with water to remove the tetrahydrofuran solution on the film surface instantly. Thus, we perform physical modeling of short-term contact of the tetrahydrofuran solution during implementation of the method using industrial printing equipment for manufacture of packaging with tactile marking.

To conduct calorimetric studies of the film structure after removing the tetrahydrofuran solution from its surface and drying to the fixed mass, we place packs of microdisks with the diameter of 2 mm to the incineration dish of the differential scanning calorimeter (DSC) PC-DSC 204 Phoenix

(NETZSCH, Germany). Standard DSC diagrams in the coordinates "sensor signal – temperature" were obtained from the samples weighing $0.5\div0.7g$ at the incineration dish heating rate of 10 °C/min.



Figure 1. Diagram for study of the unilateral effect of the tetrahydrofuran aqueous solution on one surface of the polyvinyl chloride film: 1 – heavy glass jar; 2 – sealing cover; 3 – clamp; 4 – thermo shrinkable polyvinyl chloride film; 5 – annular gasket; 6 – tetrahydrofuran solution.

3. Results and discussion

Obtaining relief characters and images that carry information on shrinkable film products, readable by a person visually and tactile, is based on the technology of interval materials [17, 19] which can be obtained from polymer films using various methods, for example, by local heat treatment under isometric conditions with hot print [20] or laser beam [21]. The interval materials have no relief and, as a rule, no difference from the initial films in color, shape and type of the surface. Subsequent thermal shrinkage of the interval materials, in gaseous or liquid heat transfer agents [16], exhibits the heat-exposed intervals in a form of local bulges of the given height and shape determined by the heat treatment of the film at all stages of the marking process (figure 2).

According to the method, proposed and recently patented in the Russian Federation [6], the interval materials and subsequent relief marking of the membranes made of thermo shrinkable films can be obtained by partial dissolving and/or local swelling of the polymer in a liquid [18], printing varnish, or ink. After the film is treated with a liquid containing a solvent that quickly penetrates (diffuses) into the polyvinyl chloride, the level of internal stresses in the thermo shrinkable polymer film decreases, the chemical composition of its ingredients, the supramolecular structure, and, as a consequence, the rate of relaxation processes during the subsequent shrinkage on the marked object also change [16]. Change of the polymer properties in the intervals treated with the solvent causes development of the relief after thermal shrinkage of the membranes or labels on the product.

Based on the measuring results of short-term tetrahydrofuran absorption from the aqueous solution by the surface of the polyvinyl chloride film (table 1), we determine conditions for the marking implementation method which provides the height and width of the relief necessary for each specific marked object (figure 2) that occur during shrinkage of the labels or membranes on objects.

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b







Figure 2. View of the marked membrane before thermal shrinkage (a, d) and after thermal shrinkage (b, c, e-h). The membrane was pre-treated in the area of the relief at 25 °C with 50% solution of tetrahydrofuran in the printing ink. 1 – thermo shrinkable polyvinyl chloride film; 2 - hidden marking; 3 - view of the marking after shrinkage on a flat former.

Solution temperature, °C	Solution concentration, %	Tetrahydrofuran absorption by the film, kg/m ³
25	30	300
	40	360
	50	380
40	30	180
	40	230
	50	290
60	30	120
	40	90

Table 1. Tetrahydrofuran absorption by the thermo shrinkable polyvinyl chloride film from aqueous solutions.

To apply the tetrahydrofuran aqueous solution to the surface of a thermo shrinkable polyvinyl chloride film, we propose to upgrade printing equipment to use the method of screen printing with a cylindrical shape [22]. Possible location of the shafts in the printing section of the screen printing equipment and the movement pattern of the "printed" thermo shrinkable film are presented in figure 3.





It is necessary to modify the screen printing equipment to increase contact time of the thermo shrinkable polyvinyl chloride film with the ink containing tetrahydrofuran and its thermostatic control at the temperature that ensures the most rapid absorption of the solvent by the polymer accelerating relaxation of internal stresses of the film [16]. Contact time of the thermo shrinkable polyvinyl chloride film and the ink is increased by manufacturing of a cylindrical printing plate with big diameter and the maximum possible coverage by the film.

Coverage of the screen printing plate by the film is not currently used in traditional printing processes on paper and film materials [22].

Increase of contact time of the thermo shrinkable polyvinyl chloride film with the solvent can be carried out using, for example, intaglio or screen printing machines by passing the film through a heated table or extended drying conveyor where diffusion of tetrahydrofuran into the polymer and the stress relaxation process at the printed areas continue together with removal of excess solvent from the film surface (figure 4).

After application of the liquid, containing a solvent of polyvinyl chloride, to the film through the metal mesh of the screen printing plate, under the action of mobile tetrahydrofuran molecules diffusing into the polymer, the level of internal stresses of the thermo shrinkable film decreases, the chemical composition of its ingredients, the supramolecular structure and the rate of relaxation processes also change. This is confirmed by the results of the polymer thermophysical properties study using the method of differential scanning calorimetry (DSC) at the solvent treated sections of the film (figure 5).

The process of sample preparation for the DSC study is as follows.

Samples with the size of 10×10 mm are completely immersed into the 50% THF solution under isometric conditions at the temperature of 25 °C for 5 minutes. After the sample is taken out from the solution and the excess fluid is removed, the sample is dried under normal conditions for 120 hours, crushed and sealed in the perforated incineration dish of the calorimeter.

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Figure 4. Schematic diagram of the Rotatek Brava 450 screen printing machine sections with a heated table: A – film unwinding section; B – paint application section; C – film heating section; D – absorption and marked film drying section. 1 – thermo shrinkable film; 2 – film roll; 3 – printing cylinder; 4 – plate cylinder (metal mesh); 5 – thermostated table; 6 – exhaust ventilation; 7 – roll of the marked thermo shrinkable film.



Figure 5. Melting thermoplastic records of thermo shrinkable polyvinyl chloride films. A – the initial polyvinyl chloride sample (1st melting); B – the initial sample of the polyvinyl chloride film (2nd melting); C – the sample of the polyvinyl chloride film pretreated by heat at 120 °C; D – the sample of the polyvinyl chloride film pretreated with the 50% tetrahydrofuran aqueous solution; A1, A2, C1, C2, D1 – melting endopeaks of the polyvinyl chloride film ingredients.

The thermoplastic record, obtained using the differential scanning calorimeter, shows that the polyvinyl chloride film contains fusible ingredients or oligomeric fractions that are washed out of the film or irreversibly amortized. Presence of fusible components in the polymer composition, forming the thermo shrinkable film, is confirmed by the endo-peaks A1 and A2 in the diagram of the first heating of the sample in the perforated DSC cell from 30 °C to 120 °C (figure 5, curve A). Absence of these endo-peaks in the second heating diagram of the sample indicates irreversible amorphization of the fusible components or their evaporation. When the film is exposed to the tetrahydrofuran aqueous solution, the fusible components are partially washed out of the polymer composition, forming the thermo shrinkable film, which is confirmed by significant decrease of the endo-peaks area (figure 5, curve D) and their merging into one endo-peak D1. Assumption of the irreversible nature of the fusible components amorphization or evaporation of the components from the film, when the sample is heated in the incineration dish of the differential scanning calorimeter, is confirmed by the thermoplastic record C (figure 5) of the thermo shrinkable film sample previously heated at 120 C.

Thus, it is appropriate to conclude that internal stresses at the areas of the membrane (label) treated with the solvent are reduced as a result of the plasticization effect of the low molecular weight liquid (tetrahydrofuran) penetrating the film and subsequently extruded by thermo shrinkage on the product forming a convex relief.

4. Conclusion

The paper shows the possibility of information recording on thermo shrinkable polyvinyl chloride membranes and films using a liquid dissolving the film or causing its rapid swelling. The graphic or textual information in the form of dots or strokes is hidden and is not visually determined without shrinkage of the film on the object (container, bottle, pipe or cable). After the treatment with a heat transfer agent – hot air, steam or water – the hidden symbols form a convex relief or a set of Braille points read by fingers. Size and shape of the relief elements are determined by concentration of the solvent, the temperature and contact time of the film with the liquid (ink) containing the solvent. The fluid can be applied to thermo shrinkable membranes and films using printing equipment the design of which is supplemented by a cylindrical printing plate of big diameter and an extended system of conveyor shafts to increase contact time of the film with the liquid ink on the printing plate and the duration of drying.

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