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Macro-mechanism of polyvinyl chloride shrink sleeves embossed marking

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ABSTRACT: Mechanism description and the physical model of shrink sleeve relief labeling are presented. Embossed letters and symbols on goods packaging are intended for people with impaired vision, capable of recognizing tactile Braille marking. Internal stresses relaxation in shrink films made of rigid polyvinyl chloride at various stages of thermal printing is quantified. Dependencies between the relief parameters, the Braille font pixel diameter, and the gap between the container and the tubular film label are established. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43691.

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INTRODUCTION

Relief images and tactile Braille markings can significantly enhance functionality, features, and applications of heat-shrinkable polymer films used for packaging and labeling. Thermomechanical method of tactile markings on shrink polymeric materials was developed using rigid polyvinyl chloride (PVC) films as an example.[1] Mechanical and relaxation properties of PVC compositions used for making heat shrinkable films[2] are determined by the chemical structure of polymer macromolecules,[3,4] along with the composition and rheological properties of plasticizers made of various low molecular weight liquids and amorphous chlorine-containing polymers.[5] Small amount of plasticizer in PVC compositions makes them unsuitable for the production of labels and films used for packaging goods and small parts due to their high brittleness, especially at low temperatures. High content of plasticizers and low molecular weight polymer additives do not allow the film to support sufficient stress levels needed to secure the label on the container and to secure connected objects in a group package. Sufficient levels of stored elastic energy and stress during shrink film production,[6] and as a consequence, reversible deformation, which manifests itself at the film heating temperature below the glass transition temperature,[7,8] are prerequisites for printing 3D Braille characters and tactile markings. In a pilot study, optimal modes of tactile films marking with different thicknesses and anisotropy of internal stress and shrinkage were established.[9] However, the mechanisms of the relief formation during films shrinkage and the cause of the one-sided relief direction toward the heat source during local thermomechanical polymer treatment remain unclear.

The purpose of this paper is to study the mechanisms of relief formation during thermomechanical labeling of shrink sleeves using experimental evaluation of local deformation, relaxation heterogeneity, and shrinkage stresses in rigid PVC films. Previous studies showed that shrinking of PVC glassy polymer films, heated to glass transition temperature and 20–30 °C above the glass transition temperature, leads to a two-stage compressive stresses increase.[10] The first stress rise is due to shrinkage and stress relaxation during cooling of stressed films in manufacturing. The second stage is a result of stressed films cooling under isometric conditions. The ratio of the stresses arising in the label in two successive stages is 3:1, and their total level can reach significant 2–3 MPa values.[10] Stress relaxation and contraction in so-called interval polymer films[9] has a number of characteristics, allowing using their production technology as one of the new methods for relief marking and 3D printing. Interval materials with controlled structure and stress heterogeneity can be obtained by local heat treatment of fixed shrink films. These materials are the subject of this study and are made as follows.

MATERIALS AND METHODS

Tubular heat shrinkable film samples made of rigid polyvinyl chloride with 0.1 mm thickness were studied. The film was prepared by extruding the following molten composition: PVC suspension (PVC C-7059 M), dioctyl phthalate (DOP) plasticizer, epoxidized vegetable oil, calcium stearate, and silicone fluid (PFMS-4). Circular samples were cut from tubular shrink film. When folded, the samples had 20×52 mm^2 rectangular shape

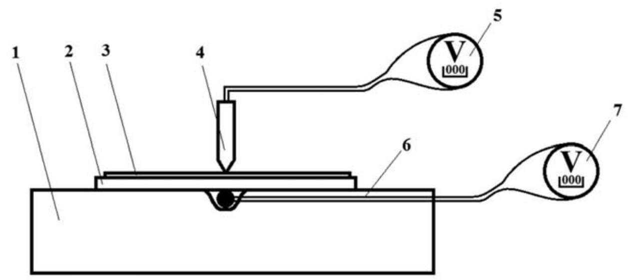

Figure 1. Schematic diagram of the device for the film local heat treatment (making Braille dots) and temperature measurements on opposite surfaces of the film. Here, 1: wooden substrate, 2: shrink film, 3: anti-sticking polytetrafluoroethylene (PTFE) liner, 4: thermostatic metal heater rod, 5: rod thermostat with temperature display, 6: thermocouple thermometer, 7: thermocouple temperature display unit.

and 104 mm initial length (perimeter). The glass transition temperature of 0.1 mm thick PVC films (manufactured by Don Polymer, Voronezh, Russia) was determined by DSC as $73 \pm 1.5\,°C$.

Annular samples were placed over the mandrel, a strip of stiff cardboard 51 mm wide, to separate the layers of the tubular film for marking them using a soldering station. The soldering station had a digital temperature display and temperature-controlled set of metal rods with 1.6–4.6 mm diameter, which heated circular tape portions under 70 psi pressure for 10 s (Figure 1).

The annular samples with local portions heated under pressure (thermally stabilized) in the form of circular spots with different diameters were removed from the mandrel, straightened and placed on movable and stationary wooden rod grips of the test bed,[11] leaving a certain gap between the rods and the film. Series of tests were conducted using the samples placed on the rods with different gap values of 2, 3, 4, 5, 6, 7, 10, 12, 15, 20, 25, 30, and 35 mm. Samples installed on the test bed were heated by hot air up to 100 °C for 400–500 s with an average heating rate of 0.15 °C/s to shrink the gap and for the relief to emerge.

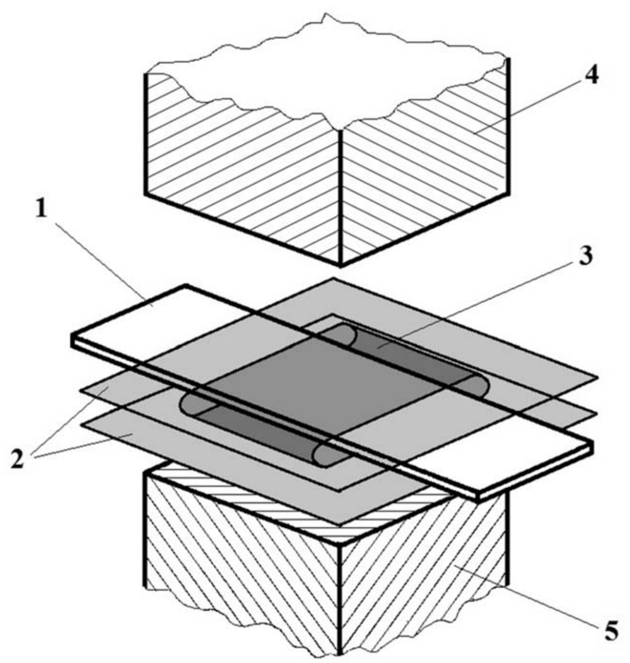

Figure 2. Physical model used to produce thermally stabilized PVC shrink film by pressing (isometric heat treatment under pressure) portions of the annular sample. Here, 1: mandrel (cardboard), 2: anti-sticking PTFE liner, 3: annular PVC shrink film, 4, 5: press plates.

For the second part of the relief macro-mechanism study, scaled models of the thermally stabilized portions (Braille dots) of the interval films were prepared, shown schematically in Figure 2. Annular PVC shrink film (3), with 20×52 mm^2 folded rectangle size, were firmly placed on a rigid cardboard mandrel (1), shielded (covered) by a thin heat-resistant anti-sticking polytetrafluoroethylene liner (2) and placed between the massive press plates (4 and 5), preheated to a certain temperature.

Hot plates pressed the film under 70 psi pressure for a few seconds, which corresponds to the actual thermal printing process. Thus, the entire ring-shaped sample was transformed into the thermally stabilized material, representing the physical model of the film with Braille dots. These samples were used for subsequent testing of thermomechanical deformation and relaxation properties. By changing the time and temperature of the compressed samples (physical model), shrink films with varying degrees of structure modification and different internal stress levels were obtained.

RESULTS AND DISCUSSION

It has been previously established that geometrical parameters of the relief formed by heating films in liquid or gaseous media depend on the anisotropy of the polymer material and local thermomechanical heat treatment mode (hidden thermal printing).[9] Moreover, heating mechanically unconstrained film for the relief to appear resulted in warped and unsightly embossed imprint. To maintain planarity of prints or their cylindrical shape, corresponding to the shape of the packaging, which is particularly important for labels, heat shrinking is proposed to be carried out directly on the product or the rigid material substrate.

The total stress generated in the film, due to its fixed surface limited shrinkage and cooling, monotonically decreases with the gap between the film and the container.[10] In practice this stress usually remains high enough to keep the stretched label on the container. However, the relief formation during film shrinkage is limited and strongly depends on the perimeters ratio of the contacting bodies, or the gap between the sample and the ring-shaped strain gauge holders in model experiments.

If the film shrinkage before full contact with the strain gauge holders is less than 30% of its maximum value, the tactile relief is not formed (Figure 3). This was experimentally observed in annular samples when the gap was less than 15 mm in Figure 3.[10]

Increasing free shrinking percentage up to 50% of the maximum (when the gap size is 22 mm) allows obtaining relief with 0.3–0.6 mm height, depending on the modified film length, which is sufficient for producing Braille dots of standard size.[12]

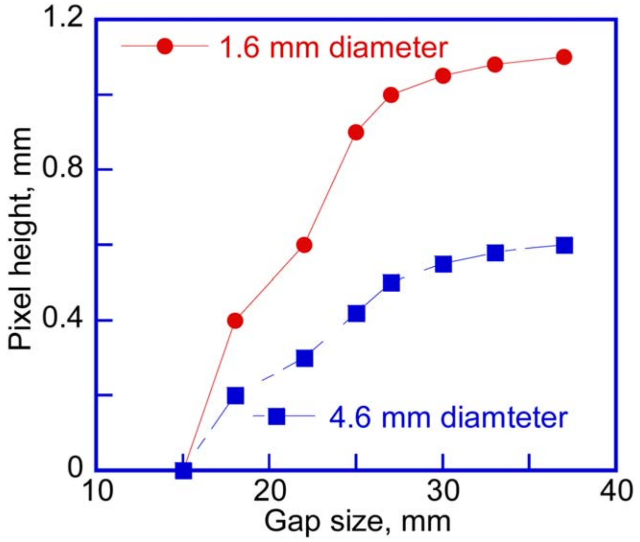

Figure 3. Braille dot height dependence on the gap for 1.6 and 4.6 mm diameter pixels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

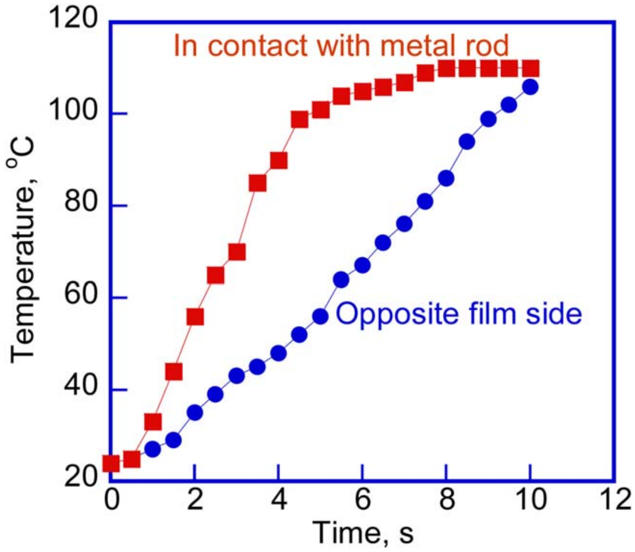

Figure 4. PVC film surface temperature in contact with metal heater rod and on the opposite side of the film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

The relief height strongly depends on the thermally stabilized zone size in Figure 3 and the film thickness. The height of 1.6 mm diameter Braille dots, obtained under identical 3D printing conditions on 0.1 and 0.45 mm thick PVC shrink films was 0.4 ± 0.03 mm and 1.1 ± 0.05 mm, respectively. Other investigated industrial shrink films made from different glassy polymers, i.e., PET and PS produced by Dongil Chemical, Alfaterm and Bilcare were 50 and 70 μm thick, respectively. Braille 1.6 mm diameter dots height was 0.5 ± 0.02 mm and 0.9 ± 0.03 mm, respectively.

In the developed relief printing method, with other parameters kept the same, the film thickness determines the physical conditions and the actual temperature inside the polymer and on the opposite side of the substrate material. Since application of pressure and heat is quite brief (1–5 s), the temperature inside the polymer is significantly different from the surface layer of the film. If the surface in contact with the metal rod is heated to the 65 °C PVC glass transition temperature and the polymer goes into the highly elastic state in 3 s, the surface on the opposite side of the film remains glassy, incapable of internal stresses relaxation for over 6 s.

The actual temperature of the polymer film surface and inside the polymer film can be different from the measured values in Figure 4, since a thermocouple can cause delays and temperature distortions associated with the glass transition temperature spikes due to the introduction of the thermocouple in the softened polymer and local reduction in film thickness.[13] However, measured data confirm the assumption of a significant film temperature difference on its opposite surfaces and, accordingly, the conditions of relaxation processes during thermal printing.

Internal stresses in the thermal stabilization contact zone with a metal heater relax much faster than the stresses in the polymer bulk and on the opposite surface of the film. This is why the relief printing is always facing the contact surface with a metal heater. To explore the macro-mechanisms and determine the physical nature of the relief appearance in interval shrinkable materials, modified fully thermally stabilized ring-shaped samples, described above, were prepared.

Film samples of fixed length were heated to 100 °C under 70 psi pressure in a press for a few seconds and cooled on a rigid cardboard mandrel. Obtained heat treated and original shrink film samples were heated at a constant rate using the same conditions as described in reference[11] up to 100 °C. Stress in the samples tightly fixed by the strain gauge holders was measured as the temperature was raised in Figure 5. Heat treatment of the two sample types using the same conditions allows determining

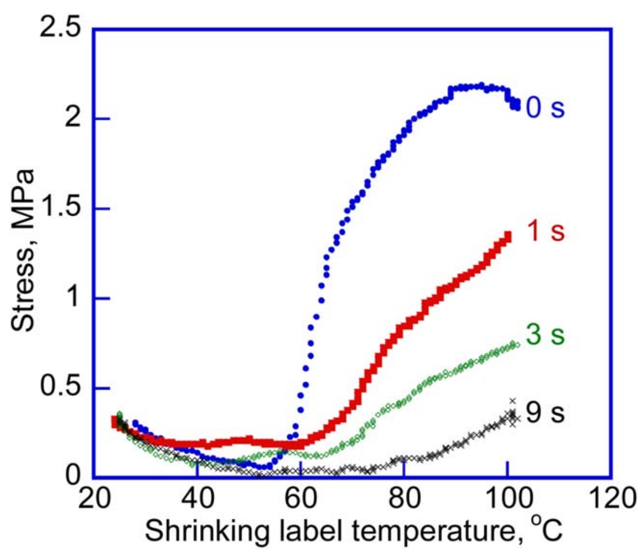

Figure 5. Stress relaxation in PVC shrink films due to constant rate heating before (0 s) and after preliminary contact press heat treatment at 130°C for 1, 3 and 9 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

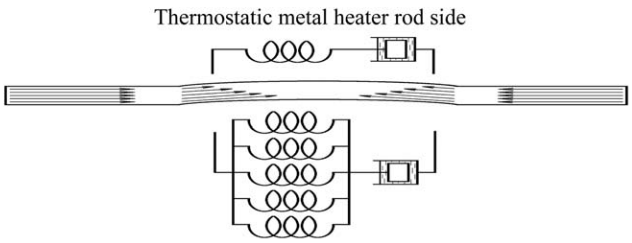

Figure 6. Distribution of internal stresses in PVC interval shrink film.

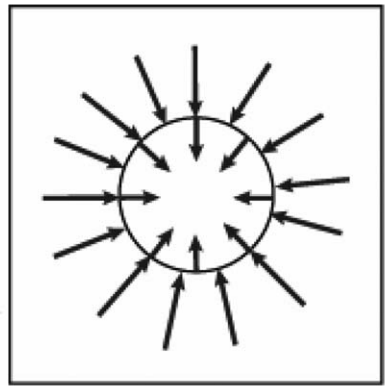

Figure 7. Compressive stresses on the back side of PVC shrink film inside and around the Braille dot arising during heat treatment in mechanically unconstrained state.

the driving forces for the relief formation on a flat shrink film. Temperature-induced stresses on the surface of modified and the original shrink films vary significantly in magnitude and temperature range.

In order to properly simulate relief printing conditions and ensure stress measurements reproducibility, the ring-shaped samples were elastically deformed using the test bed holders,[11] stretching them at low rate until the initial stress of 0.25–0.3 MPa was reached. This allows eliminating the gap and deformation of shrink films during thermal cycling. Initial stress in glassy PVC is not high and slowly relaxes at 25 ± 2 °C. Increasing the temperature to 55 °C at 5 °C/min accelerates relaxation and the initial stress level is markedly reduced by two-three times to 0.1–0.2 MPa. As PVC glass transition temperature is approached, part of the internal energy stored in the shrink film during its manufacturing by drawing and cooling is released. Tension in the original film not subjected to heat treatment is rapidly increasing, and at glass transition temperature reaches 1.5 MPa. In modified film samples subjected to heat treatment, the stress increase in this temperature range is much smaller. The difference in stress levels between loaded original and thermally stabilized samples differs by an order of magnitude, reaching 1.1–1.2 MPa in the absolute stress values. This stress difference is somewhat less for the films subjected to heat treatment for 1–3 s.

As has been shown previously,[9] free unconstrained film shrinkage is 40–50% above the glass transition temperature, while the film subjected to full isometric heat treatment is reduced by only 2–6%, depending on the kind of cooling and heating methods. Experiments also showed that the obtained relief can be removed by consequent heat treatment 70 ± 10 °C above the PVC glass transition temperature.

Based on the established relief formation mechanisms, its directionality and local surface temperature measuring results, the distribution of internal stresses and their role in the formation of the relief can be represented, as shown schematically in Figure 6. When a portion of a film is pre-treated by a hot recording element with a temperature higher than the PVC glass transition temperature, internal stresses in the polymer surface layer relax to the minimum value or disappear completely. Thus, the obtained films are sufficiently stable under normal storage conditions.[9] There are still internal stresses present inside the polymer film and on the opposite side of the thermal treatment locations during thermal printing that can cause shrinkage, but their level is much less than the stress level in the original film (label material).

Using the Maxwell viscoelastic model[14] and knowing the difference between the compressive stresses on different sides and portions of the film, macro-mechanism of the relief printing can be described, identifying the cause of its one-sided appearance. The difference between the shrinkage stress levels in parts of the film is reflected by a different number of elastic elements in the physical model. Plastic properties of the film during thermostatic pressing and free shrinkage are reflected by an equal number of viscous elements in Figure 6. Driven by the elastic forces released during heating of the whole film, the back side of the film shrinks much more and pushes the modified areas on the front film surface with low internal stress.

The following equation was used for the semi-quantitative adequacy assessment of the Maxwell viscoelastic model applied to PVC shrink films:

$$f_{el} = f_{el}{}^{0} \times\ e^{-t/\tau}, \tag{1}$$

where f_e is the stress in the shrink film, f_{el}^{0} is the initial stress prior to relaxation, t is the observation time and τ is the relaxation time. A modified laboratory bench, which allowed measuring stress in ring shrink samples during isometric and isothermal conditions was used.[11] Unidirectional compressive stress relaxation time in PVC shrink film heated to 100 °C under isometric and isothermal conditions was 82 ± 2 s. Unidirectional compressive stress relaxation time in the model of PVC shrink film sample pre-heat-treated and compressed as in Figure 2 was 142 ± 3 s. This ratio of relaxation properties and compressive stresses on respective opposite sides of the film is depicted in Figure 6.

Distribution of stresses in the planar area of Braille dots can be represented by a schematic shown in Figure 7. The distance between the force vectors, which indicate the direction of compressive forces around the local heat treatment site, is significantly less than the distance between the force vectors in the future relief protrusion (Braille dot). This difference in the distance between the force vectors corresponds to the difference in the stress measured using model film samples in Figure 5 at 100 °C. The stress can be four to five times higher on the film side in contact with the heating element. The difference in the compressive stress inside and outside of the heat treated areas on the reverse film side is much lower or negligible. Internal stress inhomogeneity on the opposite sides of the film after heat treatment determines the direction of bending towards the heater when the film temperature is increased above the glass transition temperature. Subsequent cooling fixes local film bending by the polymer glassy state. This is how the relief is formed during heat treatment of mechanically unconstrained PVC films. Printed relief can convey graphic or textual information for people with poor or impaired vision.

CONCLUSIONS

Relief printing is based on the difference between the magnitude and time of local processes of stress relaxation and shrinkage deformation in interval shrink films made of rigid PVC. Relief images and Braille font are formed on the film side in contact with the heated printing element, provided consequent thermally stimulated local dimensions shrinking of at least 30%. The proposed method of relief printing can be utilized to record and store information by using tactile symbols, also allowing completely erasing them from the sealed material by global heat treatment at a temperature higher than the PVC glass transition temperature by $70 \pm 10\,^{\circ}C$.

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REFERENCES

1. Konovalova, M. V.; Kondratov, A. P.; Nazarov, V. G.; Benda, A. F. Presented at 46th Annual International Conference on Graphic Arts and Media Technology Management and Education, Athens and Corinthia, Greece, May **2014**.
2. Bigg, D. M. *Adv. Polym. Technol.* **1990**, *31*, 101.
3. Pi, H.; Guo, S.; Ning, Y. *J. Appl. Polym. Sci.* **2003**, *89*, 733.
4. Du, H.; Zhang, J. *Colloid Polym. Sci.* **2010**, *288*, 15.
5. Wu, D.; Wang, X.; Song, Y.; Jin, R. *J. Appl. Polym. Sci.* **2004**, *92*, 2714.
6. Berstein, V. A.; Egorov, V. M. Differential Scanning Calorimetry in Physical Chemistry of Polymers: Physics, Chemistry, Analysis, Technology; Ellis Horwood: New York, **1994**; p 320.
7. Oleinik, E. F.; Rudnev, S. N.; Salamatina, O. B.; Shenogin, S. V.; Kotelyanskii, M. I.; Paramzina, T. V.; Nazarenko, S. I. *E-Polymers* **2006**, 366, *29*.
8. Shegonin, S. V.; Hohne, G. W. H.; Salamatina, O. B.; Rudnev, S. N.; Oleynik, E. F. *High Mol. Compounds A* **2004**, *46*, 30.
9. Kondratov, A. P. *Mod. Appl. Sci.* **2014**, *8*, 204.
10. Kondratov, A. P.; Volinsky, A. A.; Zhang, Y.; Nikulchev, E. V. *J. Appl. Polym. Sci.* **2015**, *133*, 43046.
11. Kondratov, A. P.; Zachinjaev, G. M. In Testing and Measurement: Techniques and Applications: Proceedings of the 2015 International Conference on Testing and Measurement Techniques (TMTA 2015), 16-17 January 2015, Phuket Island, Thailand; Chan, K., Ed.; CRC Press: London, **2015**; pp 73–76.
12. Braille dimensions, Available at: http://www.blista.de/download/druckerei/braille-dimensions.pdf; accessed on 25 March **2016**.
13. Yang, Y.; Thompson, G.; Song, J.; Hiltner, A.; Baer, E. *J. Appl. Polym. Sci.* **2009**, *112*, 163.
14. Gottstein, G. Physical Foundation of Materials Science; Springer: Berlin: **2004**, pp 239–241.