Polyvinyl chloride film local isometric heat treatment for hidden 3D printing on polymer packaging

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ABSTRACT: A method of 3D embossed printing is proposed where both point and line images can be printed on rigid polyvinyl chloride (PVC) shrink films without any consumables, such as paints, primers, dampening solutions, or washes. Embossed lettering and symbols on packaging are intended for people with poor vision, but capable of tactile marking recognition and reading Braille. This 3D printing is based on reversible deformation and stress relaxation in anisotropic glassy polymers by local isometric heat treatment of thermoplastic films under pressure. Films can be protected from counterfeiting by hidden markings due to time separation of information recording onto the film and displaying this information for visual or tactile reading. The results quantify the rate of internal stress relaxation in PVC shrink films at various stages of 3D printing, including tactile sign formation conditions. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2016, 133, 43046.

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INTRODUCTION

Various modern 3D printing methods can form embossed images of polymers on flat substrates, including various polymer films, and in most cases use thermoplastic consumables.1 Embossed 3D images can also be formed without thermoplastic consumables by cold or hot stamping using vacuum or blow molding blanks from any thermoplastic polymer.2

The novelty of presented 3D printing process compared with conventional polymer film relief forming techniques2 and 3D printing1 is that costly molds are not necessary for new combinations of characters. The 3D printing process is localized to a small area (5–10%) of the film surface and does not require heating the whole film above the glass transition temperature with subsequent fast cooling. Controlled spontaneous relief formation on the polymer film surface in an inhomogeneous compressive stresses field has not been previously investigated, thus the effects described in this article are quite valuable for practical applications.

The following sequential steps are used in various thermoforming manufacturing technologies for changing the shape of polymer films and sheets. The whole polymer work piece or its portion is heated above the glass transition temperature (the softening point), mechanically deformed by bending or stretching, and then cooled or chemically cross-linked to fix its shape. Operation modes are determined by the polymer’s thermal characteristics and reactivity, along with the possibility of simultaneous relaxation and chemical processes occurring in a short time. Embossed tactile relief on the film obtains its final shape after cooling. This kind of 3D printing for packaging material labeling is called explicit3 and only performs informational functions. Explicit labeling can be copied and easily reproduced on any packaging material to hide counterfeit (fake) goods in the package.

The proposed method of hidden labeling or “watermarking” of shrinkable materials is bifunctional and resistant to forgery.3 It has a different 3D printing operation sequence. Thermomechanical treatment of the polymer film only affects certain parts, and is carried out under isometric conditions, which is achieved by fixing the sample edges and/or because of the higher glassy polymer stiffness around the heat treatment zones. After cooling to the glass transition temperature, the film with hidden markings remains flat and does not differ from the original or the unmarked areas. The 3D printing effect is manifested by heating...
the whole film above the glass transition temperature to achieve shrink fitting (Figure 1). Figure 1 shows an example of the polyvinyl chloride (PVC) film with the Braille markings. The embossed 3D markings appear on the label after shrink fitting. The label is made of the rigid PVC film, and the 3D printing process is explained as follows. Polymer film areas, subjected to local thermomechanical modification under isometric conditions at higher temperatures than the shrink fitting temperature, have different structure and shrink at different rates compared with the entire film. As a result, modified regions warp or bend, forming embossed 3D label structures. The appearance of hidden labeling during heat treatment of the package or a special insert into the package helps to identify its authenticity.4

Understanding the nature and controlling restructuring processes in glassy polymers at various 3D printing stages is impossible without considering polymer glassy structures,5 film deformation mechanisms,6 and the surface microstructure changes during thermally assisted shrinkage.7 The aim of this article is to determine optimal conditions for local isometric processing of PVC films, ensuring sufficient thermally assisted shrinkage of the annular labels on cylindrical container with simultaneous Braille 3D printing.

MATERIALS AND METHODS

Samples of annular heat shrinkable film made from rigid 0.1-mm-thick PVC were studied. The film was prepared by melt extrusion with the following composition: polyvinyl chloride suspension (PVC-S 7059M), dioctyl phthalate plasticizer, epoxidized vegetable oil, calcium stearate (technical grade), and silicone fluid (PFMS-4). Standardized manufacturer-reported transverse shrinkage is more than 40% (“Don-Polymer” Ltd., Voronezh, Russia).

Annular samples were cut from the folded sleeve, which had 20 × 53 mm rectangular folded size, as shown schematically in Figure 2(a). The ring was spread over two wooden rods, as shown in Figure 2(b), connected to the load-measuring test frame, which allowed controlling the gap between the rods. The film sleeve was folded flat, forming an acute angle at the opposite ends, which were aligned against the rods as shown in Figure 2(b). Wooden rods with 5 mm diameter were used for thermal isolation between the test frame’s metal parts and the polymer sample since the metal frame can be quickly heated and has a different temperature than the polymer.

Round symbols were printed at 70 psi on parts of the ring-shaped shrink film samples, corresponding to the Braille letters, as described previously.9 The film was mechanically pressed with the metal roller heated to 100°C using the previously described device.11 In Figure 1 example, the modification process represents local heat treatment of a narrow 1.5–2 mm zone of the PVC film for 0.5–2 s at 85–100°C with a subsequent retention interval under pressure, and consequent cooling to the temperature below the polymer vitrification temperature.

Tests were conducted using the film ring samples placed on the wooden rods with different gap values of 1, 2, 3, 4, 5, 6, 7, 10, 12, 14, and 15 mm, as shown schematically in Figure 2(b). Samples mounted on the test frame were heated to 100°C by hot air for 400–500 s with an average heating rate of 0.15°C/s. Then the samples were kept at 100°C for 200 s, after which the heating chamber was opened and the heat-treated samples were cooled down to room temperature in 25 min. Temperature was recorded using temperature sensors and two thermocouples in close proximity to the upper and lower parts of the sample. The shrinking film was observed through a transparent window in the heating chamber.9 As the sample size reduced due to heating, tactile marks appeared with increasing load due to film shrinkage. Sample stress and temperature variations with time are shown in Figure 3.

Measuring the degree of unconstrained sample shrinkage and embossed 3D character identification were conducted in two ways, parallel with the thermomechanical tests using the load-measuring test frame.9 The first way was by means of short 30–60 s sample immersion in hot transfer fluid, which does not cause PVC swelling (water or glycerin). The second way was by irradiation with an infrared heat source inside the packet laminator (Prolamix HR 330D, Germany).10 Planar dimensions and height of the embossed 3D features along with the shrinking values were measured at different temperatures using an optical microscope.

Figure 1. PVC label fragment with the Braille markings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. (a) The front and (b) the side views of the sample positioned on the wooden rods of the testing frame for measuring thermomechanical properties of the polymers.
RESULTS AND DISCUSSION

Several successive and later simultaneously occurring interconnected relaxation processes take place in the polymer, depending on the method of fixing the shrink film. There is a slight decrease in the initial stress when the sample is heated at 30–40°C below the glass transition temperature. Tension in the sample arises due to the release of internal stress accumulated in the glassy PVC label when heated to the glass transition temperature during production.\textsuperscript{12–15} There is an additional stress in the glassy PVC label when heated to the glass transition temperature.\textsuperscript{12} The effect of stress reduction during heating is in good agreement with the theoretical concepts of the macromolecular mobility and mechanisms of stress relaxation in strained polymers.\textsuperscript{8} Polymer shrinking during thermomechanical processing with hidden markings is significantly lower and occurs at lower stress levels, as will be shown later. This difference causes bending of the local film and uplifts the modified label zones above the film’s original surface, forming tactile marks (Figure 1).

In industrial applicators, ring-shaped shrink sleeve labels are placed on the containers while moving fast along the conveyor belt,\textsuperscript{16} which is only possible if there is a gap between the label and the packaging, specified by the applicator manufacturer,\textsuperscript{16} the minimal gap is 2 mm and can be up to 15 mm, depending on the container size. Therefore, tubular film samples were tested with a gap between the holder and the label varying from 0 to 15 mm with the 130 mm ring circumference.

Due to the transverse contraction of the ring width and increasing thickness of the film in Figure 2(b), the true stress after shrinking $\sigma_{\text{true}}^{\text{shrink}}$ is

$$\sigma_{\text{true}}^{\text{shrink}} = \frac{P}{2h_{\text{shrink}}b_{\text{shrink}}} \quad (1)$$

Here, $P$ is the maximum load, $h_{\text{shrink}}$ is the film thickness after shrinking, and $b_{\text{shrink}}$ is the actual ring sample width after shrinking. True normal compressive stress in the middle of the shrunk film ring after heating to 100°C and cooling to 25°C is listed in Table I as a function of the gap size. The maximum true stress reaches 0.63 MPa in Table I without the gap. This stress consists of the 0.38 MPa stress arising during film shrinking, and Additional True Stress Due to Cooling $\sigma_{\text{true}}^{\text{cool}}$.

Table I. True Normal Compressive Stress in the Middle of the Shrink Film Ring During Heating to 100°C and Additional True Stress Due to Cooling to 25°C

<table>
<thead>
<tr>
<th>Gap $\Delta$, mm</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film width $b_{\text{shrink}}$, mm</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Film thickness $h_{\text{shrink}}$, mm</td>
<td>0.12</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.14</td>
<td>0.15</td>
<td>0.16</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>True normal stress during heating to 100°C $\sigma_{\text{true}}^{\text{shrink}}$, MPa</td>
<td>0.38</td>
<td>0.32</td>
<td>0.28</td>
<td>0.23</td>
<td>0.20</td>
<td>0.12</td>
<td>0.08</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>Additional true stress due to cooling $\sigma_{\text{true}}^{\text{cool}}$, MPa</td>
<td>0.25</td>
<td>0.12</td>
<td>0.12</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.10</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Total true normal stress $\sigma_{\text{true}}^{\text{total}}$, MPa</td>
<td>0.63</td>
<td>0.44</td>
<td>0.40</td>
<td>0.34</td>
<td>0.31</td>
<td>0.23</td>
<td>0.18</td>
<td>0.11</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Figure 3. Temperature and engineering stress of the PVC film during isometric heating and cooling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
shrinking at 100°C and the additional stress increase of 0.25 MPa during cooling to room temperature.

In Figure 3, the engineering stress was calculated by dividing the load measured using the device described in Ref. 8 by the original sample cross-sectional area. As seen in Figure 3, the engineering stress in the shrinking film reaches the maximum value at 100°C. This stress does not change much with time, and remains at the 0.35 MPa level. However, the true stress reaches 0.63 MPa in Table I. During subsequent isometric cooling of the constrained film, there is an anomalous effect of increasing the engineering stress,9 which cannot be interpreted using well-known visco-elastic models. Physical explanation of this effect is beyond the scope of this article, however, this additional engineering stress can reach 60–70% of the heat shrinkage stress, and needs to be accounted for when choosing a container, which can be deformed by the label due to excessive compression.

The shrinking-induced true tensile stress arising upon heating the film to 100°C monotonically decreases with the gap size in Table I and is substantially lower than the true stress under isometric conditions. Additional stress compressing the cooled label is comparable with the stress arising from heating the shrink film, but practically does not depend on the gap magnitude until 10 mm in the 1–12 mm range.

When testing mechanical properties of polymer films in tension by following ASTM D882 or ISO 527-3 standards, engineering stress is calculated. The true stress in the film is normally higher than the engineering stress since the cross-sectional area of the sample decreases with increasing sample length. However, comparative evaluation of the engineering and true stresses during heat treatment of shrink films in this article revealed an opposite effect. The true stress is less than the engineering stress since the cross-section of the film increased during shrinking. In Figure 3, the maximum engineering stress is 0.67 MPa, while the maximum true stress is 0.63 MPa without any gap. During heating and shrinking the film can increase its width without changing the thickness, narrow, and thicken or modify both dimensions with the increase of the cross-sectional area (Figure 4).

Irreversible change in elastic and relaxation characteristics of shrink films after isometric heat treatment is due to qualitative changes of PVC long-range order. These changes can be determined by differential scanning calorimetry (DSC). DCS data show that rigid PVC composition used for the production of heat-shrinkable film has both amorphous and crystalline structure. The degree of polyvinyl chloride crystallinity of 5–7% is low. However, the presence of the crystalline phase greatly influences the shrink film properties. Crystallites fix the stress–strain state of the macromolecules and provide elastic strain energy stored in the glassy polymer during directional drawing used for shrink films production.7,15 Short-term heat treatment of the film surface with metal tool heated to 100–110°C during the first stage of 3D printing causes melting of the crystals and thus reduces the overall internal stress level. It is well known that PVC crystallization proceeds at extremely slow rate, which is confirmed here by DSC. The initial degree of film crystallinity is only partially restored after 100 or more days. For this reason, locally heat-treated areas of the film are completely amorphous, and have substantially lower stress levels compared with the rest of the film.

When simulating the 3D printing process using the device,8 the true stress in PVC shrink films increases monotonically with the thickness and the width of the film in the central portion of the annular sample, which depends on the gap size in Table I. During the actual experiment, lateral contraction of the sample (width reduction due to film shrinkage) is distorted because of the friction between the label and the container. Thus, instead of the calculated true stress, the total measured tensile load on the label is present in Figure 5 after shrinking and cooling.

In field experiments conducted with tubular PVC 40 mm labels fixed on glass containers by heat shrink fitting, tensile loads...
were measured at different gap values. Plotting the load as a function of the gap size in Figure 5 shows that initially the total load on the container-chilled label contracting during cooling after heat shrinkage is 5 ± 0.5 kg. However, further load increase for the gap of more than 12 mm is sharply reduced by 0.5 kg with a consequent gap increased by 1 mm. These results have practical significance for selecting the optimal ratio of the container and the label dimensions to ensure reliable connection and the subsequent separation in the recycling process.17

Obtained results form the basis of a new way of 3D tactile marking on film packaging for food, drugs, hazardous, and flammable liquids, and household chemicals, etc. The marking is intended for primarily blind and visually impaired people to warn them under isometric conditions was measured. The maximum true stress at 100°C is 0.38 ± 0.1 MPa, while during cooling additional true stress is 0.25 ± 0.05 MPa, and depends on the size of the gap between the label and the container in the 0–15 mm gap range. A new way of 3D tactile packaging marking can be used for food, drugs, hazardous, and flammable liquids and household chemicals packaging intended for blind or visually impaired people.

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