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Macrostructure of anisotropic shape memory polymer films studied by the molecular probe method

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Abstract

An anisotropic copolymer film of vinyl chloride and vinyl acetate, which has shape memory properties, was investigated by the molecular probe method, thermomechanical analysis, and scanning calorimetry. It was found that the amorphous-crystalline structure and the stress–strain state of the surface layer of the film differ from the structure and state of the inner layers. The molecular probe (limited diffusion of a solvent into the surface layer of the film) revealed the localization of the elastic deformation energy of a film, which was rapidly cooled in a stressed state during production. It is shown that destroying/crushing the stressed macrostructure of the film surface via plasticization and dissolution of the copolymer, eliminates the effects of the elastic energy release during thermally stimulated shrinkage.

KEYWORDS

amorphous-crystalline structure, anisotropic polymer film, differential scanning calorimetry, diffusion, shape memory effect, sorption, vinyl chloride copolymers

1 | INTRODUCTION

Polymer films, fittings, tubes, and capsules made of materials with a remotely controlled shape, called the shape memory effect (SME), find various applications in the life and economic activities of a modern person. The stimulus for deformation is a change in temperature or composition of the environment, exposure to electromagnetic radiation, or visible, UV, or infrared light. The term shape memory material, or shape memory polymer (SMP), is often used to denote this type of stimulus-responsive material.

In medicine, SMPs are used as shells for dosage forms that provide accurate, targeted delivery of a physiologically active substance to the desired place in the gastrointestinal tract.[1–5] Deformation delayed in time without an increase in volume is manifested by a change of two or three varying directions, due to a change in temperature, chemical composition, phase, the environment, or its state of aggregation. If the deformation of these materials is structurally limited, such as one dimension being fully fixed, then the SME manifests itself as either significant internal stresses, the formation of microcracks (causing its cracking), a change in transparency, or the shift of the absorption spectrum of polarized light.[6–9]

The deformed structure of an SMP after cold stretching is fixed in space by at least two types of macromolecular interactions; one being more sensitive to environmental factors (subject to destructive action) than the other. The most resistant interactions are chemical bonds and crosslinking between polymer macromolecules and their nodes. Crystalline formations and the supramolecular structure in the amorphous part of the polymer are less stable. Moreover, the factors of external influence weaken one of the types of intermolecular interaction only in a certain interval of intensity, beyond which the difference between the forces of intermolecular interaction does not induce a macroscopic shape change.

The transformation of macromolecules and the phase change of SMPs, under the action of an active solvent, is shown schematically using an example of crystallizing thermoplastics in Figure 1. The locations of the adhesions of macromolecules due to the formation of the crystalline phase are denoted with black rectangles.

The film thickness is conditionally divided into three layers, which structure differs in the copolymer crystalline phase fraction and the degree of tortuosity of the macromolecular chains. This difference is a result of the two-stage orientational stretching when obtaining films with shape memory, including the stage of its calibration and quenching in contact with a steel cooler plate for fast cooling of one surface of the stretched film. Fast cooling of the film causes the polymer glass transition, suppressed crystallization, and relaxation of the film surface tension and ensures elastic energy conservation in the film.

In carbon-chain thermoplastic polymers, interlocking loops of macromolecules prevent their affine deformation during stretching and increase the rigidity of the polymer body.[10] The places with “rigid” connections of macromolecules (loops and crystallites) are connected by flexible chains of macromolecules in the form of sinuous lines. With tensile deformation, the tortuosity of the lines decreases, which corresponds to the straightening of the polymer chains.

When stretching the polymer film, training the shape memory, the distance between the straightening chains of macromolecules decreases, while the number of centers, and the forces of mutual attraction increase. In the

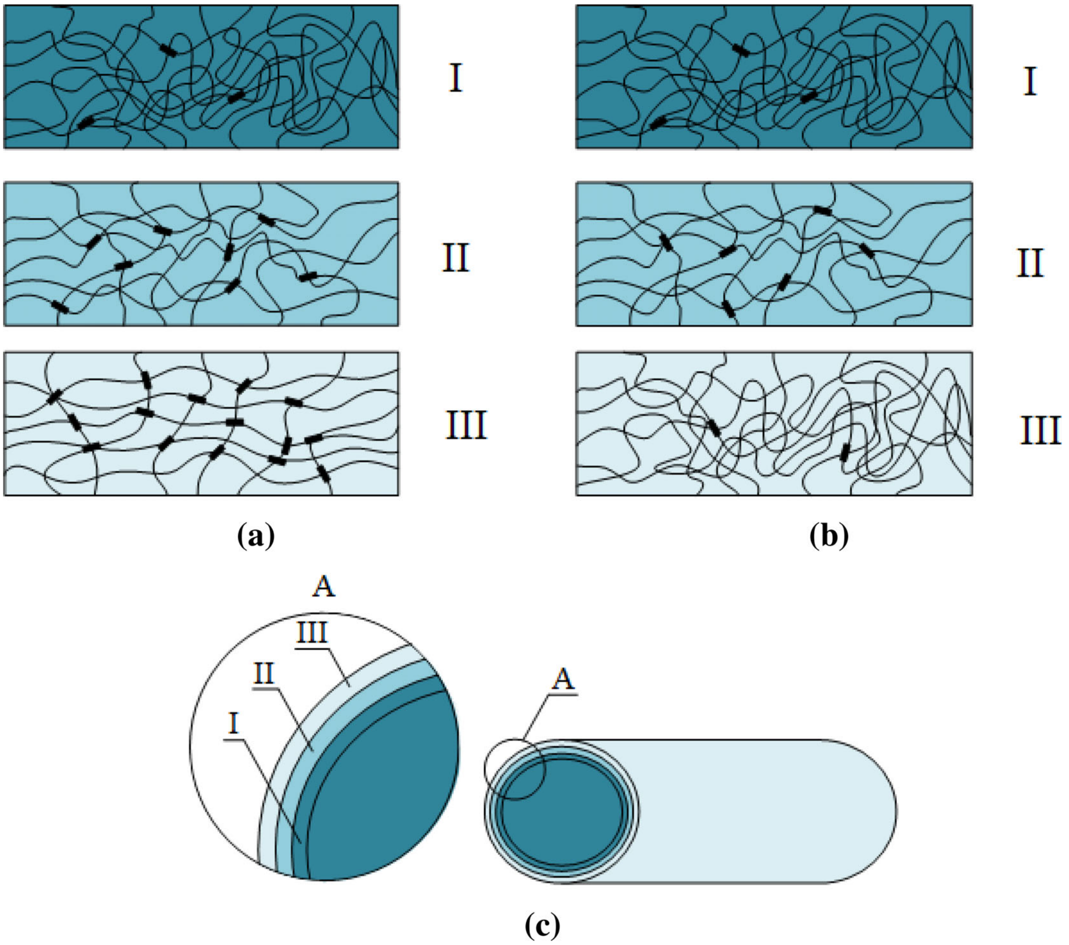

FIGURE 1 Illustration of the gradient of an amorphous-crystalline structure of an SMP (a) before and (b) after exposure to an active solvent on the outer surface of the film, and (c) conditional division of tubular polymeric heat-shrinkable film (shell) into three layers in thickness [Color figure can be viewed at wileyonlinelibrary.com]

areas of the densest chains, crystalline formations appear or additionally form with decreasing temperature, effectively fixing the shape of the polymer body in a new stress–strain state. The degree of crystallinity of the polymer is different inside the material versus on the surface layer of the SMP film. Based on the experimental evaluation of the crystallinity of the surface and inner layers of the heat-shrinkable film, the gradient of macromolecules along the thickness is depicted in Figure 1.[11]

The material in this study is a copolymer of vinyl acetate and vinyl chloride, with the glass transition temperature, T_g, 40°C higher than the operating temperature. The degree of crystallinity of stretch-oriented films is less than 1%.[12] Strong interactions between the molecules of vinyl chloride and vinyl acetate provide resistance to external influences and impart the SME. These interactions are caused by the nodes of the mechanical linking of macromolecules. Several publications are proposing physical and mathematical models for the phenomenological description and quantitative assessment of the SME in SMPs with the varying chemical composition.[13–18]

To the authors' best knowledge, the macroscopic dimensions (length of mechanical bonds) of viscoelastic elements along the direction of the orientational stretching of polymers, as well as their transverse distribution (through the film thickness) have not been considered. The role of the macrostructure of polymer bodies in determining the SME has not been discussed in the literature and has not been experimentally investigated yet.

1.1 | Purpose of the study

The purpose of this study was to experimentally verify the application of the molecular probe method in (1) determining the role that scale factor plays in the SME, and (2) indirect estimation of the viscoelastic element distribution in heat shrink films. This study aims to (3) substantiate the possibility of generating tactile marking via a short-term liquid treatment of SMPs, such as heat-shrinkable castings and labels.

This will be accomplished by direct measurement of the shrinkage force (without reducing the overall size) when immersed in a heated water bath to estimate the level of internal stresses in the shrink film. The level of internal stresses on the surface of the film is reduced by local plasticization and acceleration of stress relaxation in the copolymer with a “good” solvent, tetrahydrofuran (THF). This also reduces the glass transition temperature of the copolymer due to the partial dissolution of the surface layer from the short-term treatment of one side with a THF solution under isometric conditions.

Differential scanning calorimetry (DSC) and direct measurements of the shrinkage force were used to estimate the level of internal stresses in films post-treatment. In order to determine the degree of surface crystallinity, the surface layer was separated from the copolymer film in both the initial and plasticized states.

1.2 | Methods and procedures

A heat-shrinkable polyvinyl chloride film (PVC LF-T147/07 T25, manufactured by Klockner Pentaplast, Germany) with an initial thickness of 40 μm and a flat sleeve width (semi-perimeter) of 120 mm was used as the copolymer. A solution of analytical grade THF and distilled water (30 vol% THF) was used as the solvent. Short-term surface treatment of the copolymer films was carried out as shown schematically in Figure 2.

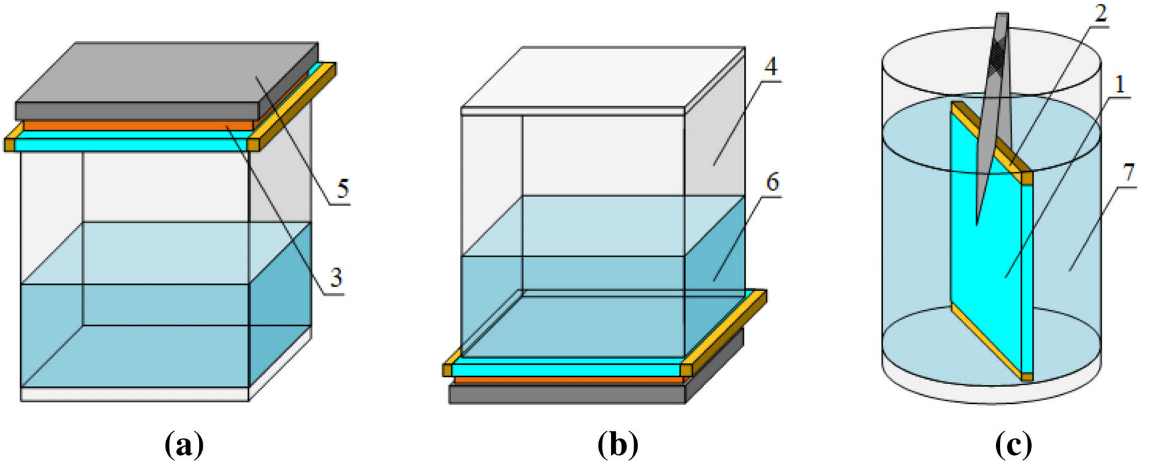

FIGURE 2 Schematics of the study of the THF unilateral effect on the one surface of PVC film in isometric conditions: 1 - PVC film; 2 - mandrel; 3 - sealant; 4 - glass jar; 5 - sealed cover; 6 - THF solution; 7 - water. (a) Original and final orientations; (b) whole setup flipped to expose one side of PVC to THF; (c) test setup post-treatment [Color figure can be viewed at wileyonlinelibrary.com]

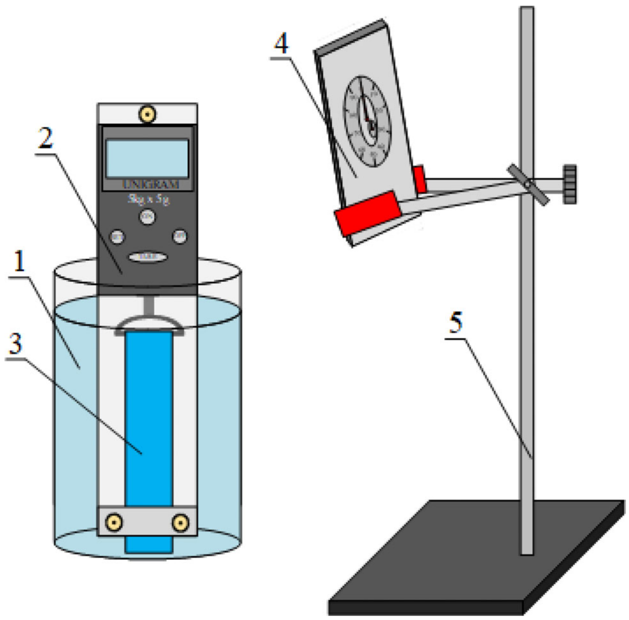

FIGURE 3 Setup for measuring shrinkage stresses in films with shape memory. 1 - water heated to 80°C; 2 - electronic dynamometer with an annular holder for a heat-shrinkable film sample; 3 - shrink film tape (ring-shaped sample); 4 - slow-motion video camera; 5 - tripod [Color figure can be viewed at wileyonlinelibrary.com]

In order to study the short-term effect of THF on PVC films with fixed dimensions, the method from reference [19] was adapted to enable accurate recording of the contact time and dimensions of the film samples (this is an isometric regime of film swelling and/or partial dissolution). To comply with isometric conditions, a sleeve of PVC film was fixed inside a thin but rigid mandrel. The sample was then placed over the opening of a large square glass jar prefilled with THF solution and sealed with a sealant and lid on one side as in Figure 2(a). This setup was then flipped upside-down for 1–10 min, temporarily exposing only one side of the PVC film to the THF in Figure 2(b). The sample was removed from the square glass jar and immediately submerged in a round container with distilled water to instantly dilute the concentration of THF on the film surface in Figure 2(c). To maintain a constant temperature of the THF, the massive jar was placed in a water bath at 40 ± 1°C. Physical modeling of the process and precise recording of the THF contact time with PVC are essential.

The film was heated above its T_g by immersing the samples with fixed lengths in distilled water at 80°C. To measure the force of the film shrinking, a device was set up consisting of a rigid base and two clamps, one of which was connected to a dynamometershown in Figure 3. The dynamometer readings were obtained by video recording to determine the maximum value of the film contraction force.

Differential scanning calorimeter (DSC, PC - DSC 204 Phoenix, Netzsch Germany) was used for calorimetric studies of the untreated polymer shrink film structure. Round film samples were stamped out with a diameter of 2 mm, original thickness, and a mass of 0.1–0.12 g. When studying the structure of the treated polymer film, the top layer (0.1 mm thick) was scraped off with a sharp blade repeatedly moved perpendicular to the film fixed on a rigid substrate in one direction. The resulting small "shavings" of treated polymer, also weighing 0.1–0.12 g, and the stamped untreated micro-disks were separately placed into the perforated DSC crucible. The thermograms were recorded at a crucible heating and cooling rate of 10°C/min.

2 | RESULTS AND DISCUSSION

Short-term contact of the THF aqueous solution with the surface on one side of a copolymer PVC film was studied via the "molecular probe" method. The time-dosed local plasticizing effect on the surface structure of a strained polymer in its glassy state was observed. It is assumed that the "good" solvent molecules initially diffuse into the amorphous part of the surface layer of the copolymer, leading to its structural plasticization and a decrease in the T_g according to the Kargin-Malinsky rule.[20] Consequently, this leads to an abrupt increase in the mobility of macromolecules. The level of internal stresses causing heat shrinkage of the SMP film is reduced in treated samples. The amount of stress reduction depends on the magnitude of the sorption of THF from the aqueous solution and the penetration depth of its molecules into the copolymer volume.

In Figure 4, the amount of low-molecular-weight liquid penetrating the surface layer of the film is given as a fraction of the maximum sorption of a THF, rather than in absolute units of sorption coefficient (g/cm^3), when the film is completely immersed for a long time to saturation. This was done to confirm the hypothesis about the localization of elastic energy on the stressed film surface. The film is then cooled to a temperature below the T_g of the copolymer. This process of training the polymer and then reheating realizes the heat-responsive SME in the PVC film.

Figure 4 confirms that a small amount of solvent penetrates only into the surface layer of the polymer in a glassy state, which sharply reduces the film tension during heat shrinkage. Therefore, the authors use the term "molecular probe" as the tool to assess film surface stress localization.

To confirm the hypothesis about the localization of elastic energy on the surface of the film, a calorimetric

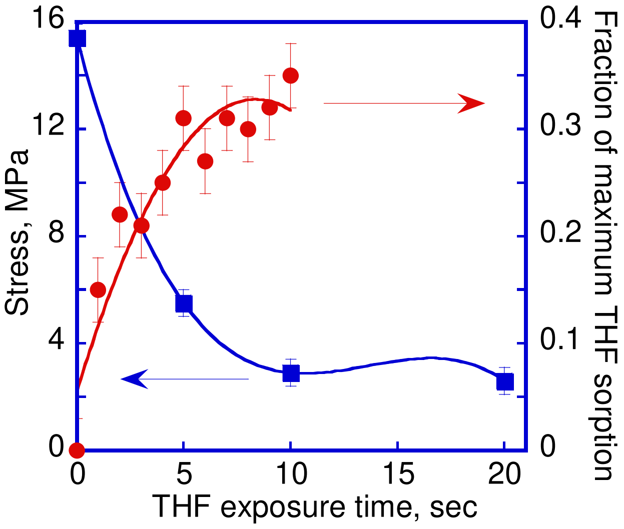

FIGURE 4 Film stress after unilateral contact with a 30% aqueous solution of tetrahydrofuran at 40°C and the fraction of maximum THF sorption [Color figure can be viewed at wileyonlinelibrary.com]

study of the mechanically removed copolymer layers was carried out with and without a short-term exposure to THF. Figure 5(a) shows the DSC diagrams of the enthalpy of PVC film which has two extrema, the same order of magnitude but opposite signs. The crystalline formation melting enthalpy is characterized by a maximum of the "endo" peak at 68°C, which corresponds to the melting temperature of vinyl acetate and vinyl chloride in the 8:1 ratio. The degree of crystallinity of the copolymer is ~0.83%.

In Figure 5(a) DSC diagrams of the samples have an "exo" peak around 50°C, corresponding to the viscoelastic energy released from the film when the SME appears in the heating mode at a constant rate.[21,22] The specific energy of this peak is 2 J/g, which exceeds the melting enthalpy of the copolymer. When the film is reheated after cooling at 10°C/min rate to room temperature, the "exo" and "endo" processes are not present in the DSC diagram, which corresponds to the absence of internal stresses (no SME) and complete amorphization of the film.[19]

Stored viscoelastic energy, which causes the SME, arises and remains in the heat-shrinkable film as a result of its training process of heating above T_g in a warm water bath, deforming it, and rapidly cooling below T_g on a metal mandrel. An abrupt increase in the viscosity of the polymer upon cooling and subsequent crystallization, fix the supramolecular structure and overall dimensions of the heat-shrinkable film.

Fixation of the film supramolecular structure occurs primarily on its surface, which is in contact with a metal cooler or a refrigerant, depending on the technology used for the film production.[23] Crystallites formed near the surface typically have about a 10°C higher average melting point (~88°C) than the average melting point of the rest of the film (~78°C). The enthalpy of fusion, which is a measure of the degree of crystallinity of the copolymer in the surface layer of the film is above the average by 20%.

The absence of an "exo" peak in the DSC thermogram of the removed surface layer of the vinyl chloride and vinyl acetate copolymer in Figure 5(b) shows the decisive role of the scale factor in the "freezing" of the elastic compression energy of the SMP. The elastic compression energy appears in the DSC thermograms as an "exo" process and causes spontaneous deformation of films upon

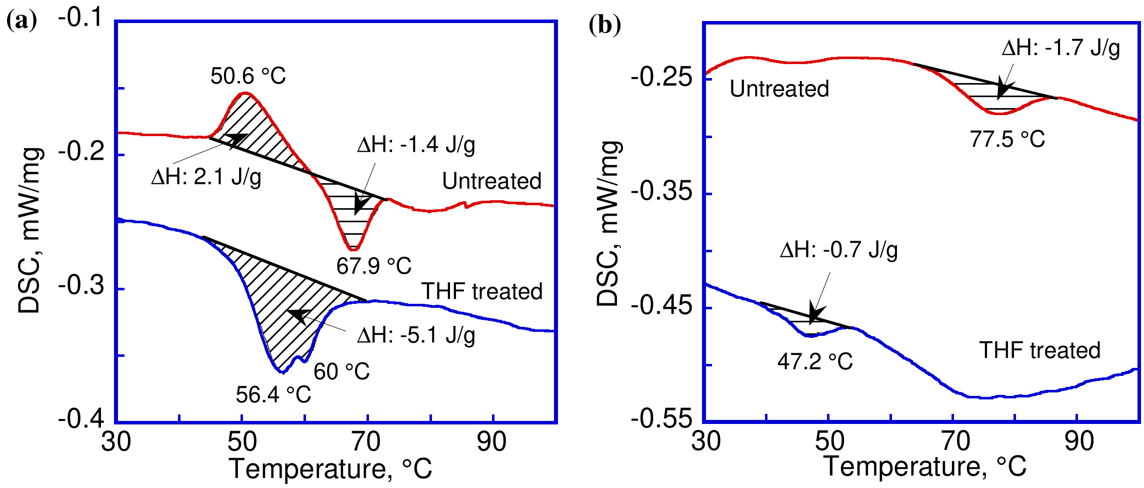

FIGURE 5 (a) DSC thermograms of untreated and THF treated PVC films; (b) DSC thermograms of the upper layers of untreated and THF treated PVC films. Samples were treated at 40°C in 30% THF solution for 10 s [Color figure can be viewed at wileyonlinelibrary.com]

heating (only in the presence of a longitudinally oriented macrostructure of viscoelastic interconnected elements).

3 | CONCLUSIONS

DSC analysis of SMP PVC films with mechanically removed surface layers showed that the amorphous-crystalline structure of the surface is significantly different from the structure of the inner layers. The difference lies in a 20% excess of the degree of crystallinity of the copolymer in the surface layer and a higher melting point, which indicates an increase in the size of crystallites on the film surface. Grinding of the PVC film leads to the loss of its mechanically stressed macrostructure, or stored SME, which is confirmed by the disappearance of the "exo" peak in the DSC diagrams.

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