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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Folding and birefringence behavior of poly(vinyl alcohol) hydrogel film induced by freezing and thawing

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Band-like folds with high aspect ratio and birefringence behavior were observed on the in situ formed thin poly(vinyl alcohol) (PVA) hydrogel film via freezing-thawing treatment of PVA aqueous solution coated on glass. The crystallite generated during the freezing of PVA solution cross-linked PVA to form the hydrogel film. The volume expansion of the hydrogel film due to the absorption of the condensed water in thawing induced the formation of folds. These folds express interesting birefringence behavior. The morphology, crystallization and birefringence behavior of the folds were characterized by polarized optical microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction. A plausible principle for the folds formation was also discussed. It has been found that the moderate interaction between the hydrogel film and the substrate and the existence of condensed water on the frozen hydrogel film played important roles in the appearance of the folds.

Introduction

Buckling is a popular phenomenon due to the mechanical instabilities triggered by thermal, mechanical or osmotic stress.^{1,2} It plays a vital role in the formation of many natural structures such as the curing-edges of leaves,³ the folds of brain tissue⁴ and friction-ridges on fingers.⁵ Buckling instabilities have been utilized to prepare variable patterns with potential application in flexible electronics, smart adhesives, microfluidic devices, microlens array and so on.⁶⁻⁹ The mostly studied buckling usually refers to bilayer systems, where two layers have different moduli or stimuli-responsive behaviors.¹⁰⁻¹⁴ There are mainly two types of the bilayer systems: the extensively studied one involves coating a rigid skin on a pre-expanded soft elastomeric sheet,¹⁵⁻¹⁷ and the relatively underexplored one of attaching a cross-linked polymer film on a rigid substrate.^{18,19} In the latter system, volume increase of the cross-linked film induced by solvent swelling will lead to compressive stress, and in most case the top film develops patters like creases or wrinkles.²⁰⁻²² However, these structures are usually shallow with low aspect ratio, which limits many proposed applications requiring high surface roughness or high local curvature. Recently, the folding structure with high aspect ratio was observed at the similar situation, where the compressive stress lead to the delamination of the film from the substrate, and the debonded free film folds upon itself to relieve the compressive stress. Tsukruk et al.^{23,24} attached a 20-100 nm thick cross-linked poly-2-vinylpyridine gel film on silicon wafer, and uniform high-aspect folded structure laying on the flat surface was formed by swelling the gel film. Folds perpendicular to the flat film was also obtained by swelling a ten to several hundred micrometers thick, cross-linked PDMS film attached on glass.²⁵

In this work we demonstrate the formation of band-like folds with a high aspect ratio, parallel or perpendicular to the flat film from a in situ formed 1-2 μm thick poly(vinyl alcohol) (PVA) hydrogel film. Different from the most previously reported buckling induced by dropping solvent on the cross-linked polymer, herein the folds just appeared by a freezing-thawing treatment of PVA aqueous solution coated on glass under humid condition. Moreover, the fold shows optical birefringence behavior observed by polarized optical microscope, which has been rarely reported for the PVA film prepared by aqueous solution casting method as the crystalline does not have adequate birefringence to be observed by polarized optical microscope except suffering special thermal treatment or melt crystallization.²⁶⁻³⁰

Experimental section

Materials

PVA with an average molecular weight of 7.7×10^4 and a degree of hydrolysis of 98% was purchased from Beijing Yili Chemical Inc. Deionic water was used as received.

Preparation of PVA hydrogel film with band-like folding structure

PVA aqueous solution (7 wt%) was prepared by dissolving the polymer in deionized water at 95 °C for 5 hours. After being slowly cooled to room temperature, the solution was spin-coated on a precleaned glass slide at 2000 rpm for 30 s. Water of 0.2 ml was sprayed in sealed vials to maintain a high humidity. The samples on glass were kept in the sealed vials and then froze at -20 °C for 1 h and thawed at 25 °C for 0.5 h. The PVA hydrogel

films without fold were prepared under a same condition but in a dry vial without spraying water. To prepare PVA bulk hydrogel, the solution was kept in a container with a depth of 2 mm and underwent the same freezing and thawing process and then dried via lyophilization for characterization.

Characterization

The optical property and the melting of the crystallites were investigated on a Nikon polarizing optical microscope (Eclipse E600W POL) with a Nikon (Coolpix4500) camera. A Linkam LTS350 hot stage was used to control the temperature. Morphology was characterized by scanning electron microscopy (SEM, Hitachi S-4300) operating at 15.0 kv. Fourier transform infrared (FTIR) spectra were recorded on a Bio-rad FTS6000/Raman III/UMA 500 system. X-ray diffraction (XRD) patterns were recorded in a transmission mode at room temperature on a Bruker D8 Discover diffractometer.

Results and Discussion

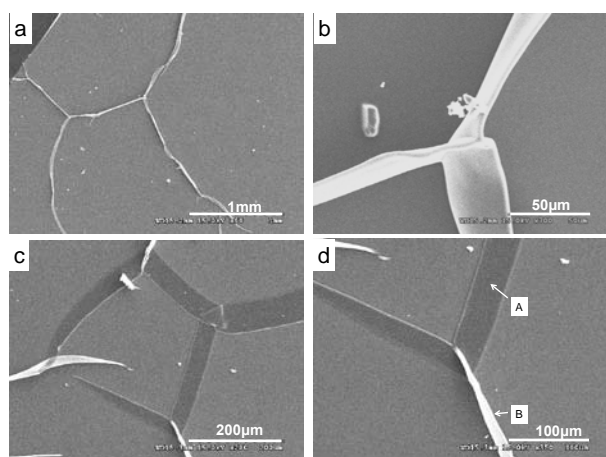


Fig. 1 SEM images of PVA hydrogel film with (a) “standing” and (c) “lying” band-like folds prepared by freezing and thawing. (b) and (d) are the magnified images of (a) and (c), respectively.

The physically cross-linked PVA hydrogels prepared by freezing-thawing method were first reported by Peppas.³¹ In the freezing process of the PVA solution, ice crystals formed and PVA was expelled from these crystals and concentrated in the interstitial sites. The high concentration of PVA was favor to form hydrogen bonds and micro crystalline sites. The as formed crystallites with an average size of about 7 nm act as crosslinker.³² The freezing-thawing of the bulk PVA solution has been studied extensively, whereas the thin PVA solution film coated on a substrate under freezing-thawing treatment has rarely been investigated. Herein, PVA aqueous solution was spin-coated on glass and then sealed in a humid vial for freezing and thawing treatment. SEM images of the resultant PVA film are shown in Fig. 1. The thickness of the dried PVA hydrogel film was about 1-2 micrometers. Interconnected band-like folds, several micrometers thick and 20 to 60 micrometers wide, can be observed on the film. The length of the fold can reach several millimeters. The fold does not always stand on the film. Part of the fold twists or lies on the surface. The “lying” region contacts with the film (part A in Fig. 1d), while the “standing” part is perpendicular to the film (part B in Fig. 1d). There are also lots of nodes in the folds (Fig. 1b-d).

For comparison, PVA film obtained by evaporating the PVA solution at ambient condition was flat without any folds.

The volume expansion induced by the absorption of the condensed water from moisture in thawing process plays a critical role for the fold formation. In a control experiment, PVA solution coated on glass was sealed in a dry vial. Freezing-thawing treatment did not induce folding. The results demonstrate that it is absorption of the condensed water that causes the self-folding.

A plausible formation mechanism of the band-like folds is described as follows. During the freezing, PVA gelation takes place and a thin PVA hydrogel film forms on glass in frozen state by using the PVA crystallites as the crosslinkers.¹⁰ Meanwhile, the moisture in the sealed vial condenses on the frozen hydrogel surface as ice particles. In the thawing process, water from these condensed ice particles is absorbed by the hydrogel film, inducing a volume expansion. The expansion of the film will be constrained by the adhesion between the film and the hydrophilic glass. Thus compressive stress is generated within the film. When reaching to a critical point, the mechanical instability induces partial debonding of the film and sharp folds with high aspect ratio are formed to relieve the stress. Nodes will appear if different folds spread and meet.²³ These folding structures persist after the evaporation of the water. Different from the ordinary swelled hydrogels, there was no crease formed on the PVA hydrogel film, the folds are formed directly from the flat state via buckle delamination.^{24, 25}

The freezing-thawing treatment in humid condition also induces the formation of folds for the as-formed PVA hydrogel film coated on glass. When the PVA solution suffered freezing-thawing treatment in a dry vial, the PVA hydrogel film was formed without fold. After spraying water in the sealed vial, similar folds appeared on the film by freezing-thawing again. Herein, the factors that affect the folding of the as-formed thin PVA hydrogel film were investigated. It is found that moderate adhesion between the PVA hydrogel film and the substrate is a crucial factor.²⁵ If the as prepared PVA hydrogel film was dried in open environment, the second freezing-thawing treatment under humid condition cannot induce folding. This can be ascribed to the strong interaction between the substrate and the PVA hydrogel film after dried. The compressive stress resulted from the volume expansion cannot conquer the interaction between the film and the substrate. Thus delamination does not likely occur. So keeping the wet state of the hydrogel is necessary for obtaining the moderate adhesion during the freezing-thawing process.

To further study the mechanism of the folding, the second freezing-thawing treatment was substituted by ordinary water swelling for the as prepared wet PVA hydrogel, via dropping water on the hydrogel surface, however, the similar folding did not occur. Though the wet PVA hydrogel film has weaker interaction with the glass comparing to the dry hydrogel, the interaction is still too strong for ordinary solvent swelling induced compressive stress to concur. Thus the freezing-thawing treatment was required. It is proposed that, during the freezing-thawing treatment, the freezing decreases the interaction between the PVA chains and the glass substrate to a degree, via excluding the PVA chains contacting with the substrate by the ice

nucleation and growth on glass, thus the compressive stress induced by water swelling is sufficient for the partial debonding of the hydrogel film and finally the self-folding occurs during the thaw process. The same process should occur for the spin-coated PVA solution, thus the freezing-thawing treatment plays a key role in the formation of the folds for both spin-coated PVA solution and the as-formed PVA hydrogel.

Previous researches mainly focused on the formation of the folding. The difference in the crystallization and optical behavior between the folding and flat area of the film was paid little attention. In this work, the optical property of the fold was investigated and an interesting birefringence behavior was found. Normal and polarized optical micrographs of the PVA film are shown in Fig. 2. It can be seen that the “standing” folds, where the polarized light can pass, display an intensive birefringence behavior, while the “lying” folds and the flat area do not. The birefringence behavior usually was caused by the anisotropic structure of the crystal or the residual stress. Here the “lying” and “standing” fold suffered similar compression and stress release, and the birefringence disappeared when the “standing” fold was put to “lying” state with the micromanipulator (Fig. S1). So the stress can be excluded as the main factor of the birefringence behavior. As PVA is a crystalline polymer, the birefringence behavior should be ascribed to the anisotropic structure of the PVA crystal.

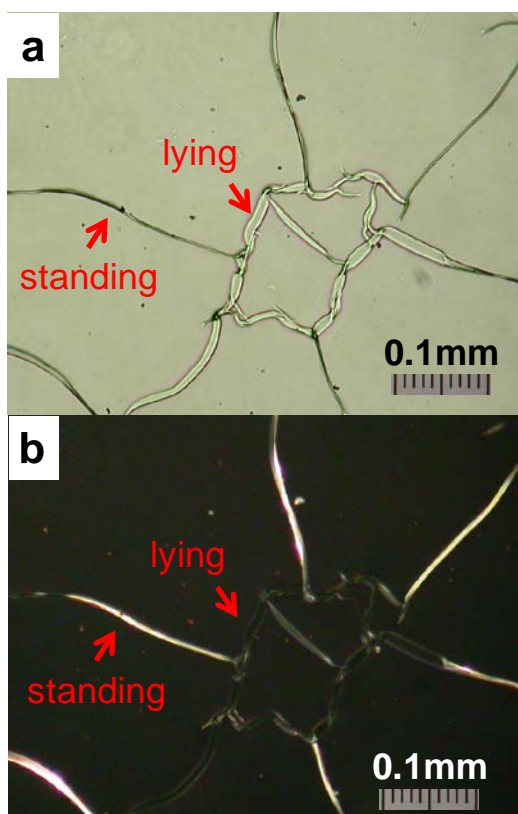


Fig. 2 (a) Normal optical micrographs of freeze-thawed PVA film, (b) corresponding polarized optical micrographs of (a). The “standing” band shows an optical anisotropic property.

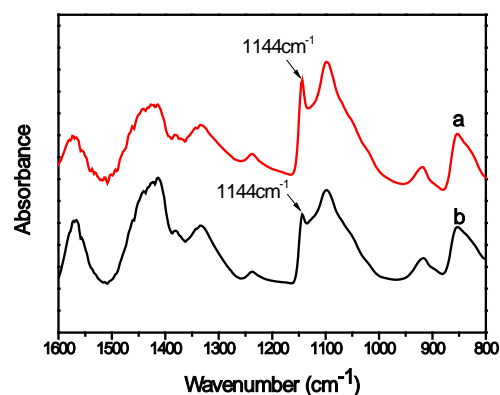


Fig. 3 The FTIR spectra of the folding (a) and flat (b) areas of PVA film.

It is difficult to compare the crystalline difference between the fold and the flat area of the film by XRD or differential scanning calorimetry because the folding occurs in micro scale. The difference of the crystallization behavior between the “lying” folds and the flat area was studied by FTIR equipped with microscope. The incident light can be focused on an area about $10 \times 10 \mu\text{m}^2$ with the assistant of the microscope, thus the FTIR spectrum on these two different areas can be collected, respectively. The FTIR spectra of the fold and flat area are shown in Fig. 3. The absorption at 1144 cm^{-1} was assigned to C-O stretching of doubly hydrogen bonded OH in crystalline domains of PVA.¹⁶ The presence of the peak at 1144 cm^{-1} for the flat area indicates the existence of the crystalline. The FTIR spectrum of the fold area has a more intensive peak at 1144 cm^{-1} , demonstrating a higher degree of crystallinity than that of the flat area.³³ These results imply that during the freezing-thawing process, crystallization happens in the folds and also the flat area, but the folds have a higher crystalline degree. The reason may be due to the volume expansion induced compression and the following stress releasing which allows the further ordered arrangement of the chains. For the folds, the “lying” and “standing” regions suffer similar compression and stress release. Therefore, we presumed they have the similar crystallinity.

The birefringence behavior was also studied by polarized optical micrographs at different temperature. The optical anisotropic phenomenon can be clearly observed at room temperature (Fig. 4a). There is no change in the optical phenomenon when the sample was heated to $230 \text{ }^\circ\text{C}$, around the melting temperature of PVA crystal.³¹ Further heated to $250 \text{ }^\circ\text{C}$, the optical anisotropic phenomenon becomes weaker and almost disappears on some standing regions while the folding structure remains, indicating the fold turns to structural isotropic (Fig. 4b).

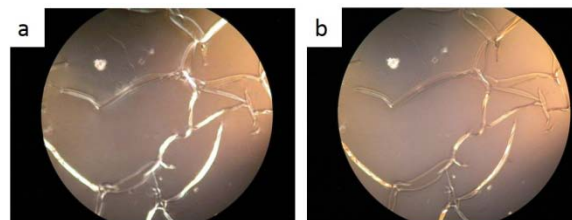


Fig. 4 In situ observation of the melting process of PVA folds on glass under polarized light. (a) Room temperature, (b) $250 \text{ }^\circ\text{C}$.

From the above result, it could be found that the birefringence

is ascribed to the crystallite in the “standing” folds. But why the “lying” fold with crystallite did not show birefringence behavior? As reported previously, the crystalline PVA in the solution casting film was found lack of adequate birefringence, so the birefringence behaviour could not be observed from the polarized optical microscopy for the flat area and the “lying” folds. But for the “standing” folds, their height is more than ten times the thickness of the flat area. In addition, the birefringence disappears when the “standing” band was put to “lying” with the micromanipulator (Fig. S1). We proposed that the accumulation of the birefringence along the height and also the sharp ridge structure make the observation of the enhanced birefringence behavior of the “standing” folds. This is consistent with that the birefringence behavior was also observed for the thick hydrogel with ridge structure prepared via freezing-thaw treatment (Fig. S2).

Fig. 5 shows XRD patterns of the PVA hydrogel film with folds and PVA bulk hydrogel, respectively. The XRD patterns show that the two samples have the same crystal structure, no new crystal structure was formed for the thin PVA solution film coated on glass under freezing-thawing treatment with high humidity.

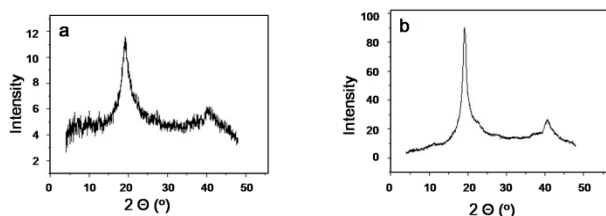


Fig. 5 XRD patterns of the PVA hydrogel film with folds (a) and bulk PVA hydrogel (b).

Conclusions

PVA band-like folds were obtained by freezing-thawing treatment of PVA aqueous solution and PVA hydrogel film on glass sealed in a humid vial. The moderate adhesion between the PVA hydrogel film and the substrate, and the volume expansion due to the water absorption played crucial roles in inducing the folding. The folding structure had a higher degree of crystallinity than the flat area. Birefringence of PVA standing folds was observed, which can be ascribed to the accumulation of the birefringence along the height.

Acknowledgements

We thank the financial support from 973 Project of China (2013CB933000) and NSFC (No. 21121001, 51073012, 51125010).

Notes and references

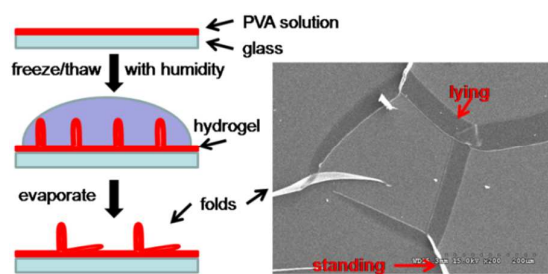
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† Electronic Supplementary Information (ESI) available: The optical micrographs of the PVA hydrogel film with folds before and after putting one “standing” fold to “lying”, the thick hydrogel with ridge structure, and their corresponding polarized micrographs. See DOI: 10.1039/b000000x/

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TOC



A band-like folding structure with high aspect ratio, parallel or perpendicular to the flat film, and birefringence behavior was observed on the in situ formed thin PVA hydrogel film via freezing-thawing treatment of PVA aqueous solution coated on glass.