Solvent induced transition from wrinkles to creases in thin film gels with depth-wise crosslinking gradients†‡

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We investigated solvent induced transition of surface instability from wrinkles to creases in poly(2-hydroxyethyl methacrylate) (PHEMA) gels with depth-wise crosslinking gradients. The mode of surface instability and morphology of surface patterns was found to be dependent on the equilibrium linear expansion, which was a function of crosslinker concentration and the solvent–polymer interaction. The maximum linear expansion was obtained when the PHEMA film was swollen in a good solvent, which had the Hildebrand solubility parameter (δs) close to that of PHEMA gels, 26.6 to 29.6 MPa1/2. In a relatively poor solvent (e.g. water), wrinkling patterns were obtained and the morphology was determined by the concentration of the crosslinker, ethylene glycol dimethacrylate (EGDMA). In a good solvent, such as alcohol and alcohol/water mixture, the equilibrium linear expansion ratio increased significantly, leading to the transition from wrinkling to creasing instability.

In an ethanol/water mixture, we systematically varied the ratio between ethanol and water and observed the transition from wrinkling to creasing when gradually adding ethanol to water, and the reverse transition when adding water in ethanol. The onset of the linear expansion ratio for creasing (αc,c) was again found dependent on EGDMA concentration: αc,c = 2.00 and 1.3, respectively, for gels with 1 and 3 wt% EGDMA. Finally, we demonstrated confinement of the creases by combining swelling and photopatterning.

Introduction

Polymer networks in the form of thin films are attractive for many applications, such as sensors,1 microfluidic devices,2 responsive coatings,3,4,5 tissue culture substrates6,7,8 and bioadhesives.8–10 In many of the applications, the polymer gels interact with a solvent. In a good solvent, the network is highly swollen. The resulting large volume change could lead to undesirable failures in the gels. Recently there has been interest in harnessing swelling induced instability to create surface patterns with controlled morphology, order, size, and complexity. It is known that the degree of swelling, and hence the volume change, is dependent on polymer chemistry, the crosslink density and the solvent quality, i.e. the affinity between the solvent molecules and the polymer chains.

When an isotropic gel is attached on a substrate, it swells preferentially perpendicular to the rigid substrate, resulting in anisotropic osmotic pressure that generates a biaxial compressive stress on the film surface. When the stress or linear expansion (α = h/h0, the ratio of swollen film thickness to initial thickness) exceeds a critical value, the gel surface buckles, generating different modes of instabilities, including wrinkling and creasing (Fig. 1).11–15 For an incompressible network, such as an elastomeric poly(dimethylsiloxane) (PDMS) coated with a thin hard skin, the compressive stress generated under bending is typically small, and formation of wrinkles with smooth and shallow

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surface undulations are often observed. When the network becomes highly swollen, such as polyacrylamide gels in water, the initially free surface begins to touch each other, forming cusps in the gel in the form of localized sharp folds, or so called creasing instability (Fig. 1b). 

Although the driving force for wrinkling and creasing is the same, the two modes of instability occur at very different critical strains, and hence, different critical linear expansions ($\alpha_c$). There have been a wide range of critical values reported experimentally, 2.0–3.7 in different materials systems. Hong et al. recently derived a theoretical onset value for creasing, $\alpha_{c,c} = 2.4$, assuming the crease formation is fast so that there is no solvent migration in the gel, thus, resembling incompressible elastomers. This theoretical prediction, however, may not always represent the behavior of a real swollen gel system. Much work in the literature has focused on manipulation of swelling-induced wrinkling instabilities in elastomeric films, and creasing instabilities in hydrogel films to form complex patterns. Few have studied the transition between these two modes of instability. Further, most of the material systems are homogeneous networks. It will be appealing to design a new material system that will continuously change the surface instability behaviors in a controlled fashion, addressing often neglected factors, such as the solvent–network interaction and solvent diffusion kinetics in the network, to the onset of wrinkling and creasing, as well as their transition. 

We have recently reported the formation of a wide range of surface wrinkling patterns by swelling poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogel films confined onto a rigid substrate simply by varying the concentration of the crosslinker, ethylene glycol dimethacrylate (EGDMA). The ability to control the morphologies of the surface patterns, ranging from random worm-like structures to peanut shape, lamellar and highly ordered hexagonal structures, lies in the creation of depth-wise modulus gradient in PHEMA gels, allowing for fine-tuning the solvent diffusion and swelling kinetics by the EGDMA concentration. The resulting surface patterns are wrinkles not creases, which are often observed in highly-swollen hydrogels. This is because water is a relatively poor solvent for PHEMA gels, thus, a lower onset linear expansion for wrinkling, $\alpha_{c,w} = 1.12$, is obtained in our system. It is possible to transform wrinkles to creases when swelling the PHEMA gradient gels with a better solvent. 

Here, we report creasing formation in the gradient PHEMA gels swelling in different solvents. Our results indicated that the equilibrium linear expansion ratio ($\alpha_c$), thus, the mode of the instability, can be tuned by solvent quality. The initially shallow undulations that appeared in water swollen films began to expand and touch each other, forming sharp folds, with addition of a good solvent, such as ethanol, in water. The onset for the transition of the wrinkling to creasing ($\alpha_{c,c}$) was found to decrease significantly from 2.0 to 1.3 with increasing EGDMA concentration from 1 to 3 wt%. The magnitude of the instability and fold depth increased with further increasing the linear expansion, and finally, the films fractured when the fold depth reached the film–substrate interface.

Results and discussion

The preparation of gradient PHEMA gels followed the procedure reported previously. Crosslinked PHEMA films were photopolymerized from a precursor solution of partially polymerized PHEMA, photoinitiators (Darocur 1173) and EGDMA. The precursor solution was cast onto a methacrylated glass slide, and exposed to UV light in open air. During radical polymerization, oxygen dissolved in the precursor scavenge the radicals generated from the photoinitiators, creating a depth-wise modulus gradient in the PHEMA film. The depth profile could be varied by the film thickness and EGDMA concentration.

When immersed in water, water diffused through the gradient PHEMA film, creating an anisotropic osmotic pressure; its profile was dependent on the crosslinking gradient. The outer gel surface becomes viscoelastic and liquid-like while the bottom layer near the substrate remains as an elastic solid. Due to the glassy nature of the dry PHEMA, the swelling-induced surface patterns are kinetically trapped upon drying, allowing us to directly visualize the swollen patterns in the dry states.

For a surface-attached film, the volumetric swelling ratio ($V$) is approximate to linear expansion ($\alpha$), which can be defined as:

$$\alpha = h / h_0 = 1 / (1 - \phi_s)$$

where $h$ and $h_0$ are the thickness of swollen and dry films, respectively, and $\phi_s$ is the solvent fraction in the network, which is dependent on the degree of crosslinking and solvent quality. The solubility parameters ($\delta$) and the Flory–Huggins polymer–solvent interaction parameter ($\chi$) are approximation of the solubility of polymers in solvents. Therefore, it is possible to vary the swelling ratio to observe both wrinkling and creasing instabilities in one single system by simply increasing the solvent quality without changing the materials characteristics, therefore, attesting the experimentally obtained critical values versus the theoretical prediction.

Previously, we found that the onset of wrinkling in water swollen PHEMA gradient films is independent of EGDMA concentration but decreases with increase of the initial film thickness. The equilibrium linear expansion ($\alpha_c$), however, decreases from 1.30 to 1.20 when increasing the EGDMA concentration from 1 to 3 wt%, leading to the transit from peanut-shaped patterns to highly ordered hexagonal structures. All these surface patterns are in nature smooth wrinkles, which are fundamentally different from the creasing patterns with sharp folds observed in the highly swollen polyacrylamide hydrogels (Fig. 1a). 

However, when the gradient-PHEMA films were equilibrated in various good solvents, including methanol (MeOH), dimethyl sulfoxide (DMSO), ethanol (EtOH) and 1-propanol (NPA) for 72 h, very different pattern morphologies were observed, suggesting creasing formation although the onset was dependent on the EGDMA concentration (Fig. 2a). To understand the swelling behaviors, we first calculated the solvating potential of solvents in different polymer–solvent systems according to the Hildebrand theory:

$$\frac{\alpha}{\alpha_{\text{max}}} = \exp \left[ \alpha a (\delta_s - \delta_p)^2 \right]$$

where $\alpha_{\text{max}}$ is the maximum linear expansion ratio, and $a$ is a constant. $\delta_s$ and $\delta_p$ are the solubility parameters for the solvent and the polymer network, respectively.
Table 1 Hildebrand solubility parameter values for different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\delta_s) (MPa(^{1/2}))</th>
</tr>
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<tbody>
<tr>
<td>1-Propanol (NPA)</td>
<td>24.5</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>26.5</td>
</tr>
<tr>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>26.7</td>
</tr>
<tr>
<td>Methanol (MeOH)</td>
<td>29.6</td>
</tr>
<tr>
<td>Water</td>
<td>47.8</td>
</tr>
</tbody>
</table>

From eqn (3), it is clear that \(\alpha_{\text{max}}\) is reached when swelling the network in a solvent with \(\delta_s = \delta_p\), i.e. the highest affinity to the polymer network. The solubility parameter values for different solvents are summarized in Table 1. The \(\delta_p\) of PHEMA gels is calculated from \(\delta_p = \phi_{\text{EGDMA}}(\delta_{\text{EGDMA}} - \delta_{\text{PHEMA}}) + \delta_{\text{PHEMA}}\), where \(\phi_{\text{EGDMA}}\) is the EGDMA fraction, \(\delta_{\text{EGDMA}} = 19.23\) MPa\(^{1/2}\) and \(\delta_{\text{PHEMA}} = 29.66\) MPa\(^{1/2}\). The solubility parameters of the PHEMA gels containing 1 wt% and 3 wt% EGDMA, are 26.5 and 29.6 MPa\(^{1/2}\), respectively.

As seen from Fig. 2b, \(\alpha_{\text{max}}\) was obtained from DMSO \([\delta_s = 26.7\) (MPa\(^{1/2}\)]\), where large cracks and film detachment from the glass slide were observed within 48 h swelling. The equilibrium linear expansion decreased gradually in solvents with \(\delta_s < 26.58\) (MPa\(^{1/2}\)) but decreased sharply in solvents with \(\delta_s > 26.5\) (MPa\(^{1/2}\)). For PHEMA with 3 wt% EGDMA, a similar trend was observed as that with 1 wt% EGDMA, although \(\alpha_e\)’s were in general smaller: \(\alpha_e = 2.06 \pm 0.21, 1.37 \pm 0.15\) and \(1.15 \pm 0.11\) in MeOH \([\delta_s = 29.6\) (MPa\(^{1/2}\)]\), EtOH \([\delta_s = 26.5\) (MPa\(^{1/2}\)]\), and water \([\delta_s = 47.8\) (MPa\(^{1/2}\)]\), respectively, in comparison to \(2.25 \pm 0.17, 1.84 \pm 0.13\) and \(1.36 \pm 0.05\) from swelling PHEMA with 1 wt% EGDMA in the corresponding solvents.

To systematically study the solvent effect on linear expansion and surface pattern formation, we fine-tuned the solvating potential by using a two-component mixed solvent. We gradually changed the solvent quality by addition of a good solvent to a poor solvent or vice versa. A two-component solvent system, which has one component with \(\delta_s\) value higher and the other with \(\delta_s\) value lower than that of the solute (here, polymer network), is often a better solvent than the individual ones. For this purpose, ethanol with \(\delta_s > \delta_p\) (good solvent) and water with \(\delta_s < \delta_p\) (poor solvent) with different volume ratios were mixed for swelling PHEMA gels. The films were equilibrated in each solvent mixture for at least 30 min. The resulting surface patterns were found similar to those equilibrated for 72 h, therefore, 30 min swelling period was chosen here for the rest of the study.

The equilibrium surface patterns of gradient-PHEMA films (with 1–3 wt% EGDMA) swollen in EtOH/water mixed solvents are shown in Fig. 3a. Regardless of EGDMA concentration, the initial pattern morphology changed significantly in the solvent with 40 vol% EtOH and no major change of pattern size and morphology was observed with EtOH vol% further increased up to 80 vol%. For gels with 3 wt% EGDMA, the equilibrium pattern morphology in water was hexagonal with long range order, which gradually transformed to a mixture of hexagonal pattern and peanut-shaped pattern (both smooth wrinkles) with 20 vol% EtOH, then to needle-shaped crease patterns in 40 vol% EtOH, which remained up to 80 vol% EtOH (Fig. 3b). For 1 wt% EGDMA, the original peanut-shaped patterns transformed to needle-shaped patterns in 20 vol% EtOH and then into star-shaped patterns, typical indication for creasing instability, in the mixed solvent with 40 vol% EtOH. However, a decrease in pattern size, and change of pattern morphology was observed in pure ethanol, suggesting de-swelling of the film. These results were in good agreement with the equilibrium expansion ratio values obtained from the confocal depth profiles (see Fig. 4): \(\alpha_e\) increased with increasing EtOH volume fraction. For gels with 1 wt% EGDMA, \(\alpha_e = 1.3\) water, and increased to \(\alpha_e = 2\) in 40 vol% EtOH, but somewhat plateaued afterwards at 2.1 in 60 vol% EtOH and 2.0 in 80% EtOH. \(\alpha_e\) decreased to 1.8 in 100% EtOH. For gels with 3 wt% EGDMA, the \(\alpha_e\) followed the same trend as that with 1 wt% EGDMA but the values were much lower, in the range of 1.2 to 1.3. We believe that the plateau in \(\alpha_e\) may be attributed to the crosslinking gradient in the PHEMA films. As we reported before, the depth of crosslinking gradient decreases with increasing crosslinker concentration: \(~34\) μm for films with 1 wt% EGDMA and \(~27\) μm for 3 wt% EGDMA. Beyond this depth, the film becomes uniformly crosslinked and the amount of solvent diffused through the film is significantly decreased. Thus, even though the solubility parameter of the mixed solvent continued to increase with addition of EtOH, \(\alpha_e\) did not change much.

To further confirm the instability mode (wrinkling vs. creasing) in the swollen PHEMA films, we monitored the evolution of surface instabilities in situ using confocal microscopy depth...
Fig. 3  (a) Optical microscopy images showing the equilibrium swelling patterns for PHEMA gels (with 1–3 wt% EGDMA) in ethanol/water mixtures. (b) Confocal microscopy images of PHEMA films (3 wt% EGDMA) scanned in $xy$- (left) and $xz$- planes (right). Dotted lines on the $xy$- scans correspond to the location in the $xz$-scans. The dotted region on the depth profiles indicate the dynamic evolution from wrinkling (shallow undulation) to creasing instability (formation of fold). Films were first immersed in water and ethanol was gradually added to the system. Films were equilibrated for at least 30 min. in each solvent composition before scanning.
profile images (xz-scans) (Fig. 5). For films with 1 wt% EGDMA, the amplitude of the patterns increased with increasing EtOH vol%, and high fluctuations in the amplitude were observed as $\alpha_e$ approached $\sim$2.0 (40% EtOH). At this point, the linear expansion was accompanied by the transverse expansion of the swollen layer, which induced surface contacts, leading to the formation of folds or cusps in the film (Fig. 1 and 5). This $\alpha_e$ value is defined as $\alpha_{e,c}$ the onset for transition from wrinkling to creasing. For films with 3 wt% EGDMA, shallow folds appeared at $\alpha_{e,c} \approx 1.3$ (in 40 vol% EtOH) (Fig. 5 and Fig. 3b), whereas sharp folds were only observed in DMSO when film became fractured at $\alpha_e > 2$. In the reported swelling of homogeneous gels, the critical linear expansion values for creasing are in the range of 2.0 to 3.7 and independent of the crosslinker concentration. In our PHEMA gels with depth-wise crosslinking gradient, the onset for creasing was found to be dependent on the crosslinker concentration and at lower linear expansion values.

Once the fold is formed in the creases, a cusp could be either pushed out or the two neighboring cusps could merge to form a single cusp. Tanaka et al. have argued that the only way for the film to expand after cusp formation is by expansion of the cusps outside of the film, leading to the disappearance of the folds. When swelling PHEMA in DMSO for a prolonged time, we observed that the fold depth increased with further expansion, and disappeared into cracks when the compressible stresses overcame the bonding strength between film and the substrate such that the folds approached the film-substrate interface (see Fig. S1, ESI†). The onset linear expansions for fracture $\alpha_f$ was 2.82 $\pm$ 0.41 and 2.09 $\pm$ 0.14 for films with 1 wt% and 3 wt% EGDMA, respectively.

To investigate the possibility of the reversibility of the pattern morphologies between different wrinkle patterns and creases by varying solvent quality, we first kept the PHEMA films (1 wt% EGDMA) in water in the rubbery state, followed by gradual increase of the EtOH volume fraction in the EtOH/water mixture from 0% to 100 vol%, and then reversed the order from 100% to 0 vol% EtOH. The equilibrium morphology for each solvent was captured after the film was kept in the solvent for 30 min. The film initially formed smooth peanut-like wrinkles in pure water and was in transit to creases with addition of ethanol as seen in Fig. 3; the creasing instability was subsequently reversed by addition of water into ethanol (Fig. 6). The near identical equilibrium pattern morphologies during swelling (Fig. 3) and deswelling (Fig. 6) processes with identical EtOH vol% suggests that the transition between wrinkling and creasing was almost reversible except that the morphology of 0% EtOH during deswelling was not completely recovered. This may be due to residual solvent left in the film during deswelling process. Nevertheless, the location of wrinkles or creases was highly correlated from cycle to cycle. Such memory effect is in agreement with the report by Trujillo et al. on crease formation in homogeneously crosslinked polyacrylamide gels.

To further demonstrate the utilization of creasing to create complex patterns, we coupled photopatterning and solvent swelling to direct the surface instability in confined regions. As seen in Fig. 7, the PHEMA precursors were first crosslinked through a photomask with square dot arrays (diameter = 100 µm, pitch = 400 µm) (see insets in Fig. 7a,b) at the same intensity used to create the gradient PHEMA gels, followed by pattern
development and swelling in methanol. The uncrosslinked regions were washed away with methanol, during which swelling-induced patterns developed simultaneously (Fig. 7a,b) in the exposed regions. By using photomasks of opposite transparency, we directed the crease formation either within the dots (like the flower petals) or in the surrounding regions. Because light intensity through the mask has a Gaussian distribution, the center of the dots was more crosslinked than the edge of the dot, therefore, no creases formed within the swelling time (30 min.). When the film from Fig. 7b was dipped into DMSO, cracks started to appear (c), leading to the formation of square patterns for extended periods (d). Scale bars: 50 μm.

Conclusions

We investigated solvent swelling induced dynamic evolution of surface instability from wrinkles to creases in PHEMA gels with depth-wise crosslinking gradients. The maximum linear swelling was obtained when the PHEMA films were swollen in a good solvent with the Hildebrand solubility parameter, $\delta_s$, close to that of PHEMA, 26.6 to 29.6 MPa$^{1/2}$. In a relatively poor solvent (e.g. water), wrinkling appeared and the morphology was determined by the crosslinker concentration. In a good solvent, such as alcohol and alcohol/water mixtures, the linear expansion ratio increased significantly, leading to the transition from wrinkling to creasing instability. The onset of the linear expansion ratio for creasing ($a_{c,c}$) was found dependent on the EGDMA concentration. The linear expansion reached another critical value for fracture ($a_f$), where the depth of the folds approached the film-substrate interface, leading to crack formation and film detachment. The value of $a_f$ was also found strongly dependent on crosslinker concentration. Finally, we demonstrated confinement of the creases by combining swelling and photomasks.

Our study suggests that it is important to consider solvent–polymer interactions and crosslinking density of the polymer gels together with the cohesive strength of the gel to develop a full picture of swelling induced instability and its dynamic pattern transition from one mode to another. We believe the difference of the reported critical linear expansion ratios for crease formation in our system vs. the homogeneous and highly swollen gels, such as polyacrylamide, will offer new insights for theoretical study of the mechanism of instability of soft networks.

Experimental

PHEMA prepolymer was prepared by UV exposure (UVP Black Ray, 8 mW cm$^{-2}$) of 2-hydroxyethyl methacrylate (HEMA, 2mL, 98%, Alfa Aesar) as monomer and the Darocur 1173 (3 wt%, 60 μL, Ciba) as photoinitiator for 60 s. Another mixture of Darocur 1173 and the crosslinker, ethylene glycol dimethacrylate (EGDMA, Polysciences) (2 : 1 wt ratio), was added to the
viscous prepolymer to form the PHEMA precursor solution. A series of precursor solutions without and containing EGDMA (1–3 wt%) were prepared, which were stable for several months when kept in dark. ~100 μm thick PHEMA films were prepared by coating the precursor solutions on glass slides using a Micrometer Adjustable Film Applicator (S271727, Sheen Instruments Ltd., Kingston, England). Precursor coated glass slides were then exposed to UV light (Omnicure S1000 UV Spot Cure System, Exfo Life Sciences Division, Mississauga, Ontario, Canada) for 20 min. (10 mW cm⁻², 365 nm) in an open air environment. In order to prevent film delamination from glass slide during swelling, the glass slide was functionalized with 3-(trimethoxysilyl)propyl methacrylate (TMS, Aldrich) before casting the PHEMA precursor solution. The PHEMA films were swollen in different solvents, including distilled water, methanol (MeOH, Sigma), ethanol (EtOH, Decon Labs Inc.), 1-propanol (NPA, Fisher), dimethyl sulfoxide (DMSO, Sigma), and EtOH/water mixtures for at least 30 min. For photo-patterning, PHEMA precursors were exposed to UV light through a photomask with square dot arrays (dot diameter = 100 μm, pitch = 400 μm), (see Fig. 7). The dot size is larger than the wrinkle wavelength of PHEMA gels (~80 μm) with the dry film thickness of 100 μm. The photomask was placed in between the lamp and the precursor solution in close proximity to the precursor solution.

Optical microscopy was performed on an Olympus BX61 motorized microscope with Hamamatsu controller. Confocal microscopy imaging was performed on a Nikon TE300 inverted microscope fitted with a Bio-Rad Radiance 2000 MP3 system (Bio-Rad Laboratories, Inc., Hercules, CA). Images were observed through a 10× and/or 20× objective, and recorded with Lasersharp 2000 software (Bio-Rad Laboratories, Inc.). A fluorescent dye, methacyrloxyethyl thiacarbonyl rhodamine B (PolyFluorTM 570, Polysciences, Warrington, PA), was added to the precursor solution to obtain contrast (gel appeared red under fluorescent light). Depth profiles were obtained by collecting z-scans with 1 μm step size. All measurements were performed using ImageJ (1.41n, National Institute of Health).

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