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Juan Rodríguez-Hernández *Editors*

Wrinkled Polymer Surfaces

Strategies, Methods and Applications

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J.R.H. would like to dedicate this book to his father. He was a source of inspiration and motivation to become a scientist. Thank you so much.

C.M.G.H. wants to dedicate this book to her beloved mother, Catalina, who was an example of perseverance, determination, and integrity.

Foreword

Inspired by nature, many materials scientists have focused their research efforts both on understanding the mechanisms involved in the unique properties of natural surfaces and trying to mimic their behavior from a synthetic point of view.

In this context, many of the strategies reported to reproduce the superior properties of surfaces in nature failed or resorted to intricate methodologies that require the use of expensive and sophisticated equipment. In this sense, many advances in the development of polymer surfaces have been associated with technological improvements. However, more recently, several alternative approaches have been developed in which the surface patterns originated are not the result of refined fabrication techniques but take advantage of the instabilities that can be produced in polymer surfaces.

Surface instabilities are sometimes intrinsic to thin films, but may also be induced. For instance, upon heating, applying an electric field, or upon exposure to aqueous solutions at different pH values, the surface may respond by altering the initially planar surface morphology. As a result, depending on the types of stimuli applied, the external conditions and material properties can be influenced to manifest a myriad of surface patterns. It is worth mentioning that some of these would be difficult, if not impossible, to obtain by conventional surface patterning techniques.

In this context, one of the most extensively explored surface patterns produced as a result of surface instabilities is the formation of surface wrinkles. Surface wrinkles have been obtained using different materials (hydrogels, elastomers, or thermoplastics), external stimulus (heating, swelling, mechanical stretching, etc.), and film structures (bilayer, gradient, and homogeneous films). In spite of the large amount of work carried out in this area, there are only a few collections and reviews of the recent advances in this area. Thus, the preparation of this book is motivated by two reasons: first, most reviews are several years old already, and as this is a research area that develops quickly, and so are out of date; second, there is a lack of a wide overview on the subject that would assist scientists, students, and engineers who want to learn about wrinkle formation. We hope this volume will assist a wide variety of readers in acquiring relevant knowledge in this interesting and developing research area.

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Preface

This volume, entitled *Wrinkled Polymer Surfaces: Strategies, Methods, and Applications* aims to cover topics ranging from the fundamental principles of wrinkle formation up to the final application of the materials developed. As a result, this book is divided into four main sections. The first part includes the basic principles of wrinkle formation and the most extended strategies for their fabrication. The goal of this part is to establish a basic understanding of the methodologies described in the book.

The second section is focused on describing novel approaches to forming wrinkled surfaces that have not been extensively explored, yet offer unique potentials. The methodologies selected for this volume include the fronta006C polymerization/vitrification, ion-beam bombardments, interfacial swelling on thermoplastic surfaces, and the use of direct laser interference patterning.

The third part involves chapters in which originality is the focus of the material employed. Thus, in addition to the typical elastomeric foundations (described in Part 1), this part covers the use of hydrogels with a homogeneous or a gradient structure that upon the appropriate stimulus form wrinkles. Besides hydrogels, this part includes illustrative examples of the formation of wrinkles in 2D materials, such as graphene, but also in 3D materials such as elastomeric Janus particles.

The fourth part is devoted to current and potential applications of wrinkled material surfaces. In view of the large potential of these surfaces for biomedical applications, an entire chapter is devoted to this application. Moreover, a second chapter includes other relevant applications, including the elaboration of conductive shrinkable devices, fabrication of electrochromic devices, and the elaboration of sensors and actuators, to name a few.

The final chapter aims to present both the advantages and limitations of wrinkled polymer surface science. Moreover, this chapter also discusses what, in our humble opinion, will be the next frontiers in this exciting research area.

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Madrid, Spain Juan Rodríguez-Hernández

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Contents

Part III Materials Employed in Wrinkles Formation

Part IV Applications

Part I
Generalities on Surface Instabilities

Chapter 1
Introduction to Surface Instabilities and Wrinkle Formation

C. M. González-Henríquez, M. A. Sarabia Vallejos, and Juan Rodríguez-Hernández

1.1 Introduction to Surface Instabilities

The fabrication of functional and micro- and nanostructured polymer surfaces has been extensively explored during the last decades. The large effort carried out in the elaboration of these materials is justified by the wide variety of applications that largely depend on the surface properties of a particular material. For instance, both patterning and functionalization of polymer surfaces have been demonstrated to play a key role in the preparation of substrates for cell growth [1, 2] in the fabrication of microchips and microelectromechanical (MEM) devices [3, 4] or in the control of the interfacial adhesion/friction/lubrication [5] just to mention few of them.

The progresses carried out in the elaboration of functional and micro-/nanostructured polymer surfaces have been achieved using two alternative strategies. On the one hand, significant improvements have been accomplished by taking advantage of the technological advances in terms of fabrication facilities. These usually involve

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the development of novel fabrication techniques such as laser scanning [6], soft lithography [7–9], or laser ablation [10]. However, important advances have been also reached by adapting previously described techniques. This is, for instance, the case of hot embossing/molding [11–16] and also the micro-/nanoimprinting that can be today carried out in a continuous manner (roll-to-roll nanoimprinting) [17–20]. These novel or improved technological advances offered the scientist of novel fabrication facilities with enhanced resolution capabilities.

On the other hand, contrary to the abovementioned strategies that are directly associated to the use of sophisticated tools and are, therefore, expensive and time-consuming, diverse alternatives have been proposed for the preparation of micro-/nanostructured polymer surfaces. In particular, different methodologies have been reported more recently taking advantage of the surface instabilities induced in polymer surfaces to produce a wide variety of surface patterns.

Today, it is widely admitted that surface instabilities on the polymer can be produced by two alternative routes. First, surface instabilities are spontaneously observed in confined systems at the small scale since these systems are inherently unstable. Alternatively, surface instabilities can be induced in metastable films by applying a particular external stimulus including a mechanical force that can be induced in metastable films applying an external stimulus. These external stimuli include the use of mechanical force (stretching or compression), applying an electric field or simply by heating the material. Upon removal of the force applied, the relaxation of the surface instabilities toward equilibrium produces the modification of the surface structure in order to minimize the surface energy. As a result, different surface morphologies with particular geometries and shapes with nano- and micrometer size moieties can be observed.

A large amount of scientific groups are currently using surface instabilities to pattern polymer surfaces mainly motivated by the cost reduction but also due to the wide variety of complex patterns that can be achieved. These complex surface features are challenging to fabricate by using other conventional patterning techniques. Moreover, depending on the methodology employed to produce the desired surface instability, a wide variety of intriguing morphologies have been described. As has been detailed in Chap. 2, surface instabilities currently employed for the fabrication of structured surfaces can be classified into three different groups including (see Fig. 1.1) [21]:

(a) Those methodologies in which the structuration is driven by the thermodynamics: phase separation of polymer blends and block copolymers [22–25], dewetting [26–28], or template guided structuration [29–33]
(b) Those that require an external field to induce the self-assembly and later the surface structuration: thermal gradient-induced surface patterning [34, 35], electrohydrodynamic patterning [36–41], reaction-diffusion surface patterns, [42] and growth processes, aggregation and crystal growth [43] and surface wrinkling [44]
(c) Those in which the polymeric material is altered by a changing environment: water ion-induced nanostructuration [45, 46], nanobubble-assisted nanopatterning [47], and breath figs [48–52]

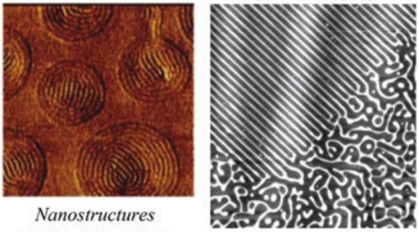
Whereas some of the instabilities on polymer films depicted in Fig. 1.1 are already widely known such as phase separation or film dewetting, others have been

a) Close to equilibrium: structuration driven by thermodynamics

Dewetting [53]

Directing convection: evaporative self-organization.[54]

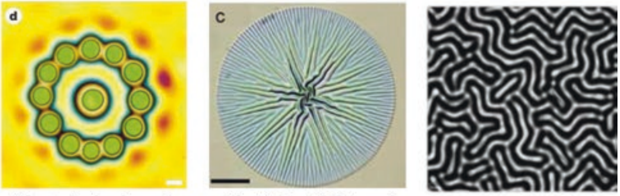
Phase separation of polymer blends and block copolymers.[55]



Nanostructures obtained by surface segregation [56]

Template guided structuration [57]

b) Far from equilibrium: Field-induced assembly

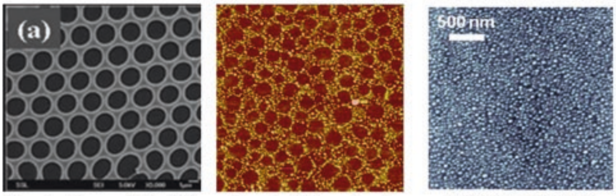


Electrohydrodynamic /Thermal-gradient induced surface patterning [58]

Elastic Instability and Surface Wrinkling [59] (scale bar 10µm).

Reaction-diffusion surface patterns. [60]

c) Polymer material reconstruction in response to a changing environment



Breath Figures [61, 62]

Nanobubble assisted nanopatterning. [63]

Water-ions induced nanostructuration. [46]

Fig. 1.1 Illustrative images of the surface patterns obtained by using different instability-based patterning approach: (**a**) structuration drove by surface/interfacial energy, (**b**) field-induced structuration, and (**c**) influence of water on hydrophobic polymer surfaces. Reproduced with permission from ref. [21]

only recently explored. The latter include the instabilities produced by using electric field-induced instabilities or thermal gradients. In spite of this, all these methodologies have been only recently employed for the fabrication of a myriad of polymer surface micro- and submicrometer size patterns. To provide a summarized overview of the different instability-based patterning techniques, Tables 1.1, 1.2, and 1.3 present the most relevant characteristics of each technique including the driving force that originates the instability, the pattern induced, the size of the surface features produced, and finally illustrative selected references from each methodology.

1.2 Wrinkling on Polymer Surfaces

Among the different patterning strategies based on surface instabilities, wrinkling instability has been the center of multiple studies as a self-organizing methodology to induce micro- and submicrometer-scale structures [44, 94]. As has been the case in other situations, nature provides unique inspiration to investigate and understand physical phenomena. Wrinkle formation is not an exception. Wrinkles appear in nature in many different forms. For instance, wrinkles appear when the skin is stretched or compressed using a mechanical force [94].

Moreover, mechanically induced surface instabilities are a central mechanism to control the development and progress of different surface patterns observed in nature [1]. Mechanically induced morphological changes are responsible for the proper functioning of different organs such as the intestine [5] or the mammalian brain [2–4]. Equally, as it is shown in Fig. 1.2, for the case of an apple, a date, and an apricot, an analogous mechanism causes the emergence of wrinkles in the course of the dehydration of fruits. Finally, as has been highlighted by Genzer and Groenewold [94], there are wrinkles with extremely large differences in length scales (more than ten orders of magnitude). For instance, mountains formed by compressive tectonic forces present wavelengths on the kilometer range. Wrinkles observed in both human or fruit skin (Fig. 1.2) obtained upon skin stretching/compression or drying respectively are in the mm length scale. Finally, synthetic systems can be prepared with wrinkles at the nanoscale. This is the case, for instance, in surface-treated elastomeric PDMS.

The formation of wrinkles at polymer surfaces is not new but rather an old observation made when using coatings. As a result, there are since the 1920s commercially available wrinkled coating. According to Genzer and Groenewold [94], pioneer workings in the formation of wrinkled coatings were done using China wood oil that was cured under atmospheric oxygen using a relatively high temperature (120–130 °C). Whereas the initial resulting coatings were somehow neglected, these materials finally lead to a new range of products known as wrinkle finishes coatings [118]. Another illustrative example of materials where the wrinkle formation was initially considered undesirable is the case of the marine and aerospace engineering during the World War II [94]. The fabrication of different elements, such as the wings, was carried out using cross-linked polymers foams having a rigid composite skin. This type of construction, known as “sandwich,” leads to buckling when a compressive external force surpasses a critical value. Buckling

Table 1.1 Close to equilibrium: structuration driven by thermodynamics

Patterning method	Driving force	Pattern induced	Typical feature size	Observations	Selected references
Dewetting	Surface forces	Isotropic, random structures (well-defined mean length scale)	Submicron (down to ~ 100 nanometers)	Occur in molten ultrathin films or films with low elastic modulus. Nucleation can destabilize thicker films	[64–70]
Directing convection	Marangoni convection/ evaporation/self-assembly	Coffee rings, polygonal network structures, fingering instabilities, cracks, chevron patterns, etc.	Nm µm size	Marangoni convection and stick-slip motion can determine the final patterns observed	[71–73]
Self-assembly and microphase separation	Phase separation of polymer blends and/or block copolymers	Random structures (polymer blends) and self-assembled nanostructures (block copolymers)	Nm to µm	Phase separation influenced by the film thickness, temperature, and substrate	[69, 74–81]
Surface segregation	Surface/ interfacial energy	Layered segregation	Nm	Block copolymer segregation from blends afford nanostructured interfaces	[56, 82, 83]
Template-guided structuration	Surface-induced structure formation	Governed by the template: hexagonal, stripes, squares	Nm to µm	Extensively employed in combination with block copolymers and blends Surface affinity assisted the self-assembly of block copolymers and blends	[29–33]

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significantly affects and reduces the mechanical properties of the part. These two examples of wrinkle and buckling served as a starting point in the investigation of the forces and surface instabilities involved in the formation of these patterns.

Pioneer investigations about the wrinkle formation mechanism based exclusively on the experimental observations on cured wood oil lead to rather a controversial hypothesis. On the one hand, Auer et al. [119] reported that UV light was at the origin of the wrinkled formation. However, on the other hand, Merz et al. [120] demonstrated that wrinkles can be also formed without using UV light. At the same time, other groups evidenced that the environmental gases such as combustion product, the

Table 1.2 Far from equilibrium: field-induced and dynamic control of surface structuration

Patterning method	Driving force	Pattern induced	Typical feature size	Observations	Selected references
Electrohydrodynamic	Electrical stress	Waves, holes, columns or channels	Submicrometer to µm	Morphology controlled by the film thickness, interelectrode distance, electrode patterning, applied field	[36–41]
Thermal gradient	External thermal gradient	Similar to electrohydrodynamic patterning	Submicrometer to µm	Morphology depends on film thickness, the gap between the plates, thermal gradient and temperature of the plates	[34, 35, 84–93]
Surface wrinkling, creasing, and folding	Mechanical stress	Controlled wrinkles	Down to µm	Wrinkle, creasing or folding orientation depends on the direction and magnitude of the applied stress	[94–105]
Reaction-diffusion	Reaction-diffusion dynamics	Hexagonal, striped, and mixed patterns	µm to mm	Patterns obtained by reaction-diffusion competition [106, 107]	[108–110]

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Table 1.3 Waterborne methods

Patterning method	Driving force	Pattern induced	Typical feature size	Observations	Selected references
Breath figures	Condensation of water vapor	Porous films with variable surface distribution and pore sizes	Hundreds of nm up to ~20 μm	Water vapor condensation during solvent evaporation drives the formation of pores. Solvent, polymer concentration, temperature, and relative humidity play a key role in the pore formation	[61, 62, 111–113]
Water ion-induced nanostructuration	Instability due to the absorption of ions at the interface	Blobs eventually self-assembled	Few tens of nm	Depend on the amount of gas dissolved in the water and the ions in solution	[46, 114, 115]
Nanobubble-assisted nanopatterning	Nanobubble-assisted nanopatterning	Nanograins, net-like nanopatterns	Few tens of nm (below 50 nm in some cases)	Surface pattern obtained in seconds	[63, 116]

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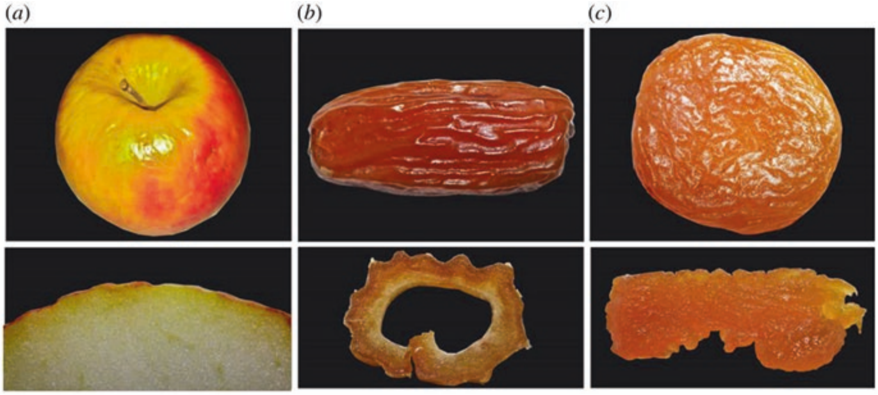

Fig. 1.2 Wrinkling instabilities caused by dehydration in an apple (**a**), a date (**b**), and an apricot (**c**). Reproduced with permission from ref. [117]

water vapor during the drying process, or nitric acid gas appear to favor the wrinkling process [121]. A similar role was played by contamination products [122–124]. As has been mentioned, all these factors prevent or favor wrinkle formation to a limited extent. However, none of them are the main cause of this process. Later studies carried out by Burrell et al. [118] demonstrated that the formation of a stiff top layer of

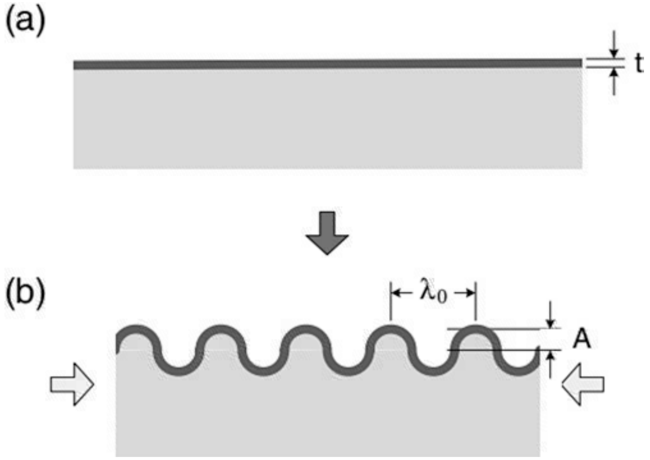

Fig. 1.3 Illustration of the general mechanisms for the formation of wrinkles in bilayered systems comprising a rigid top layer on an elastic substrate. Reproduced with permission from ref. [125]

the material promotes wrinkle formation. In contrast to previous works that assumed that the surface layer expands faster than the layers beneath the surface, Burrell et al. proposed for the first time that shrinkage and not expansion is at the origin of wrinkle formation. This excellent work is the base of the widely accepted mechanism.

In effect, the general mechanism of wrinkle formation is illustrated in Fig. 1.3 for the case of a bilayer system composed of a rigid top layer on top of an elastic foundation. The first step involves the use of a mechanical stress force (originated by osmotic pressure, stretching, or heating just to mention a few of the available mechanisms). Then, the rigid layer is deposited on top of the polymer film. Finally, upon elimination of the applied stress, the initial shape of the elastic foundation is relaxed, and at the surface a wavy structure, i.e., "wrinkles," is generated.

As will be thoroughly described in this book, without any doubt in these bilayer systems, the difference in the stiffness between the polymer surface ("skin") and the elastic polymer foundation is critical to observe this kind of patterns.

From this generally accepted mechanism, several studies have been carried out to calculate basic parameters such as the minimal force required to form wrinkles or the characteristics of the wrinkles obtained including period and amplitude. First of all, taking into account that both the top layer and the elastic polymer foundation (bulk) have their own particular elastic modulus and Poisson's ratio, the compressive force exerted on the skin can be calculated by using the following expression:

$$F = E_s \left[\left(\frac{\pi}{\lambda} \right)^2 \frac{wh^3}{3\left(1 - \nu_s^2\right)} + \frac{\lambda}{4\pi} \frac{E_f w}{\left(1 - \nu_f^2\right) E_s} \right] \tag{1.1}$$

(where h is the thickness and w is the width of the skin layer; E_s, $\nu_{s,}$ and E_f, ν_f are the elastic moduli and the Poisson's ratio of the skin and foundation, respectively; and λ is the sinusoidal deflection profile).

It is worth noting that, in the case when the load exceeds a critical value (F_c), buckling in the skin will take place. From Eq. (1.1), the wavelength of the wrinkles can be calculated supposing that dF/dλ = 0. Using this assumption results in the following Eq. (1.2):

$$\lambda_c = 2\pi h \left[\frac{\left(1 - v_f^2\right) E_s}{3\left(1 - v_s^2\right) E_f} \right]^{1/3} \tag{1.2}$$

Further studies proposed alternative methodologies to calculate the wrinkle wavelength [126–129]. In these studies, the authors evidenced that both amplitude and wavelength can be calculated taking into account an energy minimization (U), $U = U_B + U_S$ (energy due to bending (U_B) and energy due to stretching along the wrinkles (U_S)). The use of this model permitted the calculation of the wrinkle parameters. In particular, in addition to the wrinkle periodicity, (λ) permits to calculate the wrinkle amplitude (A) as follows [128]:

$$\lambda \sim \left(\frac{B}{K} \right)^{1/4} \tag{1.3}$$

$$A \sim \left(\frac{\Delta}{w} \right)^{1/2} \lambda \tag{1.4}$$

For this expression, a thin sheet with a bending stiffness B, an effective elastic foundation of stiffness K, and an imposed compressive strain Δ/W are considered.

In addition to bilayer systems, both homogeneous and also gradient substrates can produce surface wrinkling. In this case, surface instabilities are induced by film swelling (see Chaps. 4 and 5). Moreover, depending on the swelling extent, these systems can not only produce surface wrinkles but also form creases or even folding [94, 96, 130, 131]. More precisely, creases are generally observed in hydrogels supported onto a rigid substrate. In this situation, swelling limits the film, and the surface instability is produced [132, 133]. In addition, larger swelling is at the origin of eventual local delamination and the formation of buckled forms known as folded structures [134–138].

Wrinkling and a large number of alternatives to fabricate buckled structures involving surface treatments, swelling, or heating just to mention a few of them have been already described in the literature. Equally, the application of such structures has also been extensively investigated. For instance, recent examples on the use of microwrinkled surface for different applications include marine antifouling [139], responsive microfluidic channels [140], thin-film metrology [141–143], microlens arrays [140, 144], switchable wettability [105, 145, 146], flexible electronics [147, 148], tunable optical devices [140, 149, 150], dry adhesion [151], cell alignment [59, 152, 153], particle sorting [154], or the preparation of twisted nematic liquid crystal displays [155].

As will be thoroughly analyzed through this book, a large variety of strategies have been reported to induce buckling on polymer surfaces and finally produce wrinkled morphologies.

1.3 About this Book

The aim of this book is to present in a comprehensive manner the principles of wrinkle formation, the different strategies focusing on those reported recently, and of course the potential applications of such surface structures.

For this purpose, the book is divided into four sections. Part I is present the general principles of surface instabilities currently employed to fabricate micro- and nanostructured surfaces (Chap. 1) as well as to briefly present the different alternatives reported to fabricate wrinkled polymer surfaces (Chap. 2).

Part II involves a series of chapters of selected alternatives to produce wrinkled surfaces. These chapters have been selected based on the novelty of the strategies proposed. In this context, frontal polymerization/vitrification (Chap. 3), ion beam bombardment on elastic surfaces (Chap. 4), wrinkles prepared by interfacial diffusion (Chap. 5), and the use of lasers (Chaps. 6 and 7) are included in this section.

Wrinkles have been prepared using different polymeric materials including hydrogels, thermoplastics, elastomers, or even graphene-based materials. Part III covers recent examples of novel materials currently employed for the development of wrinkled surfaces. Thus, this section will describe the use of hydrogels anchored on solid substrates (Chaps. 8 and 9), wrinkles in graphene (Chap. 10), or elastomeric Janus particles (Chap. 11).

Part IV discussed in a systematic manner the most relevant applications of wrinkled polymer surfaces. Chapter 12 focuses on the bio-applications of these materials. Chapter 13 will describe the use of wrinkled surfaces for flexible electronics, and finally Chap. 14 attempts to summarize other applications in which the wrinkled surface morphology offers a clear advantage.

Finally, Chap. 15 recapitulates the most relevant aspects described in this book and provides an outlook about the future development in this particular area.

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Chapter 2
Strategies for the Fabrication of Wrinkled Polymer Surfaces

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2.1 Introduction

A large amount of work has been carried out in the fabrication of different surface patterns based on surface instabilities. In particular, the wrinkled formation is one of the most extensively explored strategies to produce surface micro- and submicrometer scale structures. In order to organize the extensive literature reported in this area, we propose the classification of the different strategies first taking into account the film structure distinguishing three different situations: layered films, gradient, and homogeneous. Thus, this chapter is organized as follows. First, we will briefly describe the possible film structures to produce wrinkled structures. Second, we will, as a function of the film structure, discuss the different methodologies and the stimuli employed to induce buckling and thus produce wrinkled surface morphologies.

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2.1.1 Films Structures of Wrinkled Surfaces

Wrinkle formation of polymer surfaces can be obtained using a large variety of different strategies [1–6] that can, otherwise, be divided and organized into three categories as a function of the structure of the precursor film. We can thus distinguish between (1) films formed by distinct layers (two or more), (2) homogeneous films, and (3) depth-wise gradient films formed by a gradual variation of the chemical/physical/mechanical properties from the surface to the bulk (Fig. 2.1).

Inside of each family, we will, in turn, subdivide into different groups taking into account the stimulus employed to induce wrinkle formation.

2.2 Layered Systems Composed of Layers with Dissimilar Mechanical Properties

Layered films are formed by two or more polymer or hybrid polymer/metal layers with, unlike mechanical properties. In order to describe the alternatives to obtain wrinkles from layered films, we will first describe the materials typically employed as substrates and as top layers including the methodologies used to achieve a rigid layer on the top of an elastic foundation. Then, we will classify the approaches reported to produce surface wrinkles based on the type of force applied to modify the form of the elastic foundation inducing the buckling of the rigid top layer.

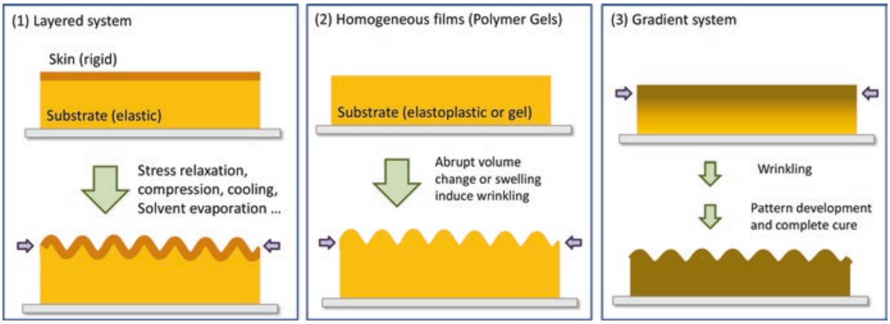

Fig. 2.1 Film structures capable of forming wrinkles: (1) Layered film structure composed of an elastic substrate and a rigid skin, (2) homogeneous films (typically homogeneously cross-linked hydrogels), and (3) gradient film with variable mechanical properties as a function of the depth. (Reproduced with permission from ref. [7])