



## Development and Characterization of Asymmetric Swelling-Induced Wrinkles on Natural Rubber Surface

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**Abstract:** Characteristics of the swelling-induced wrinkles on the surfaces of natural rubber (NR) film were investigated. The wrinkle structure was generated by swelling of NR film pre-stretched and firmly bonded onto an aluminum substrate in hexane. A novel experimental method was adopted to replicate the swelling-induced wrinkles on the NR film using an epoxy-hardener system. To get insight into the wrinkle parameters; the wrinkle length (L), wrinkle distance (D), wrinkle height (H) and the angle between two consecutive wrinkles ( $\theta$ ), the cross-sections of the replicas obtained from saturated swollen NR film were examined using an optical microscopy (OM). From the OM images, the wrinkling parameters were measured as a function of the thickness of NR film from 0.42 to 1.76 mm. Also, it was evaluated that the effects of swelling time on the wrinkling parameters. The length (L), distance (D) and height (H) of wrinkles increased as the thickness of the NR film and the swelling time increased. However, the angle between the wrinkles ( $\theta$ ) showed a sharp decrease up to a swelling time of 200 minutes and slightly decreased afterwards.

**Keywords:** natural rubber, swelling, wrinkles, replica, optical microscopy

### Introduction

Soft materials such as elastomers are the ideal option for designing micro and nano scale patterns with controlled size, order and morphology. The pattern formation and pattern replication techniques have widely used in various applications, including sensors, responsive coating, microelectronics, optics and smart adhesion. Various techniques have been employed for the fabrication of micro and nano patterns on the solid substrates. Some of them are thin film dewetting, template guided structuration, electro-hydrodynamic patterning, reaction-diffusion patterns and surface wrinkling.<sup>1-9</sup>

Surface wrinkling is a commonly observed phenomenon in everyday life and is omnipresent in nature. These naturally wrinkled systems can be found in various size and forms, such as those on human skin, the skin of dehydrated fruits and plant leaves. Recently, it has been observed that formation of artificial patterns by the wrinkling of thin films, mimicking such naturally wrinkled system at a micro/nano scale, exhibit extraordinary surface properties to fabricate smart

adhesive, solar cells, tunable devices and stretchable/flexible electronics.<sup>10-18</sup> The wrinkle structures are proposed to be beneficial in stretchable/flexible electronics owing to the abilities of the wrinkles to provide reversible stretchability and also its potential to increase electron mobility across the wrinkled surface. At high bending strain, electron mobility has been observed to increase.<sup>19-21</sup> Usually, the surface wrinkling can be artificially generated in a bilayer system comprising a thin film attached on to a compliant substrate by the application of a compressive strain.<sup>22-25</sup> The compressive strain can be induced onto the bilayer system using various techniques which include; thermal expansion, mechanical pre-strain and solvent swelling.<sup>26-28</sup>

Several researchers have investigated regarding the formation and characteristics of the surface wrinkles on thin polymeric films by employing the above-mentioned techniques. For instance, Bowden et al. for the first time investigated the patterning process of a metal coated polydimethylsiloxane (PDMS). In their experiment, a thin metal film of 50 nm thick layer of gold was coated onto a thermally expanded PDMS.<sup>29</sup> On cooling the sample to room temperature causes thermal shrinkage of the underlying PDMS

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substrate which creates a compressive stress in the metal film that is relieved by wrinkling of the top metal layer like sinusoidal waves with a uniform wavelength of 20~50 micrometer. Bowden et al. have also been generated sinusoidal wrinkling waves with wavelength from 0.5 to 10 micrometer on PDMS via thermal expansion.<sup>30</sup> In this case, they heated the PDMS and its surface is then subjected to an oxygen-plasma treatment. This treatment forms a thin silicate layer on the surface. On cooling the PDMS, it contracts, as a result, the silicate layer on the top of it experienced a compressive stress. This stress is released by wrinkling the silicate layer like sinusoidal waves. Similar to the work explained by Bowden, Huck et al. demonstrated a new method of producing wrinkles on a thin film of gold coated over a heated controlled photochemically (UV) modified PDMS substrate via thermal shrinkage of the substrate on cooling.<sup>31</sup> They have found that the selected UV (254 nm) modified PDMS surface shows a difference in the Young's modulus which strongly influences the wrinkle wavelength and geometries.

The above-mentioned methods for surface wrinkling via thermal expansion mismatch between the thin film and the substrate were not quite effective to generate highly ordered wrinkling patterns. Thus, some researchers adopted mechanical deformation in the form of a tensile pre-strain instead of thermal expansion. The pre-strain technique is an attractive way to form wrinkles since the wrinkle morphology is preserved on the sample surface after the pre-strain is removed. Volynskii and co-workers showed the wrinkling characteristics of gold and platinum coated poly (ethylene terephthalate) and natural rubber under mechanical pre-strain.<sup>32</sup> Prior to coating the gold film, they stretched the substrate and then released the film/substrate structure to generate wrinkles. Lacour et al.<sup>24</sup> and Masashi<sup>33</sup> have also employed the similar technique to produce ordered wrinkling patterns in a thin film. Takuya and Masatsugu described a reversible wrinkling pattern on platinum coated elastomeric PDMS to lateral compressive strain using a small vice under an optical microscope.<sup>25</sup> They observed the nicely ordered wrinkling patterns by applying the compressive strain and the wrinkles become disappeared when the strain is relaxed. Moreover, identical wrinkling patterns were always returned after several compression-relaxation cycles.

Swelling of a bilayer thin film/substrate with the aid of solvent or solvent vapor is another alternative way for applying a compressive strain to generate wrinkled surfaces. When immersing the layered film in an appropriate solvent, the top

polymeric film is swollen by the solvent and significantly changes its volume. As a result, the surface area of the top film tends to increase while the bottom substrate, which is being rigid in nature, remains unchanged. This condition generates an anisotropic osmotic pressure along the film thickness which imposes a compressive strain in the film. This compressive strain, once above a critical value, is released by out-of-plane deformations leading to wrinkled structures. Tanaka et al. were the first who reported the generation of swelling induced surface wrinkling patterns in an ionized polyacrylamide based hydrogels constrained on a flat substrate.<sup>34,35</sup> They have observed that the anisotropic osmotic pressure generated due to swelling increases with time as the gel swells and the pattern formation was transient in nature depending on the osmotic pressure. After the pioneering work of Tanaka et al. many researchers have focused on the formation and characteristics of swelling-induced surface wrinkling patterns in various thin polymeric film/substrate systems with an aim of developing stimuli responsive materials.<sup>27,36-41</sup>

In this paper, we report the formation and characteristics of swelling-induced wrinkle on the surface of NR film pre-stretched and attached on to a rigid aluminum substrate. The swelling-induced wrinkle was observed in different intervals up to the equilibrium swelling time as a function of thickness of NR film using an optical microscopy. A novel pattern replication technique has been introduced for the numerical evaluation of the wrinkle parameters; the wrinkle length (L), wrinkle distance (D), wrinkle height (H) and the angle between two consecutive wrinkles ( $\theta$ ).

## Experimental

### 1. Materials

Table 1 represents the formulation of the NR film used in this experiment. The used NR was STR-5CV60 (Standard Thai Rubber-Constant Viscosity 60). As per the formulation, a masterbatch was firstly prepared by mixing the NR in a Banbury internal mixer with ZnO and stearic acid at 120°C with an rpm of 60. To this masterbatch, the curative; sulphur and MBTS were dispersed well using a two roll mill. The

**Table 1.** Compounding Recipe for NR Film

Ingredient	NR	S	ZnO	S/A	MBTS
phr	100	2	5	2	1

cure time of the compound was determined using an oscillating disk rheometer (ODR-2000, Alpha Technologies, USA). The NR film was then prepared by compression molding of the compound at a temperature of 145°C under 2.5 tons of force.

## 2. Fabrication of the NR film with swelling-induced wrinkling pattern

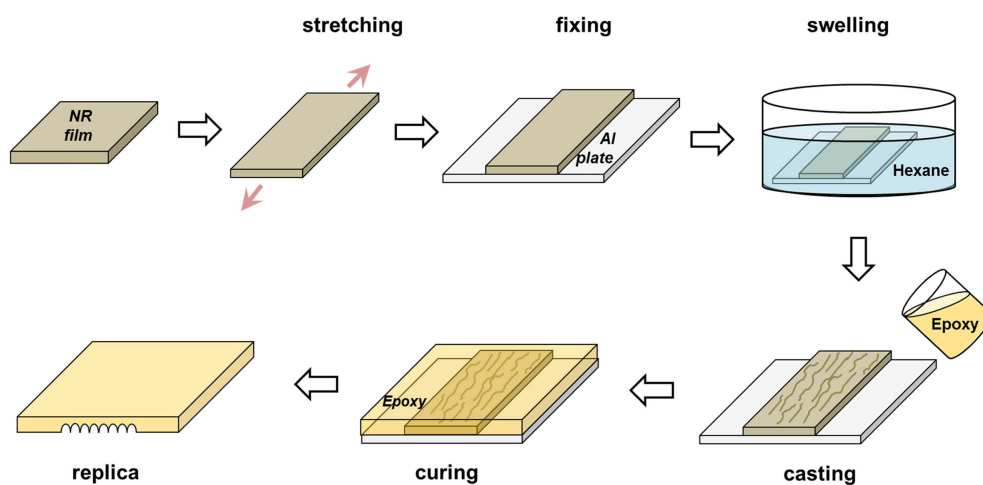
To fabricate the NR film with swelling-induced wrinkling pattern, we first prepared NR film with different thickness of 0.42, 0.77, 1.08, 1.34 and 1.76 mm. The NR film was uniaxially stretched (20% pre-strain) and attached onto an aluminum (Al) substrate using super glue. The NR film/Al substrate was then allowed to swell to an equilibrium swelling level in a suitable solvent. Here, hexane (obtained from sigma Aldrich, USA) was selected as the solvent based on the solubility parameter. After the swelling, the film was taken out for observing the wrinkle formation induced by swelling. A schematic representation of the fabrication technique is depicted in Figure 1.

## 3. Replication of wrinkles using epoxy-hardener system

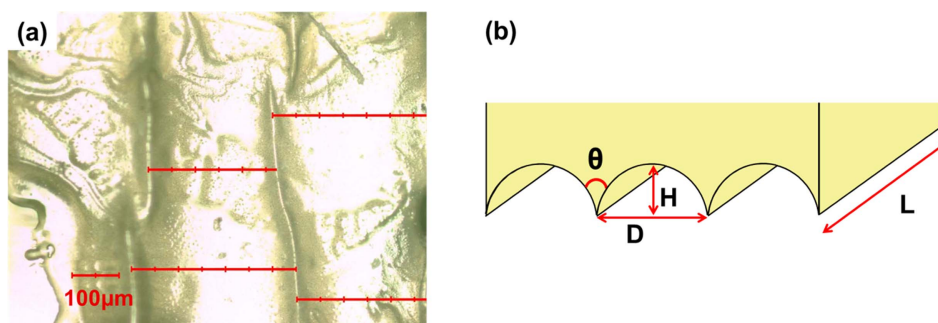
It is very difficult to analyze in detail the swelling-induced wrinkles on the surface of NR film/Al substrate due to the fast evaporation of the solvent from the swollen NR film. To circumvent this problem, a pattern replication technique has been adopted here. After a pre-determined time of swelling, the swollen NR film/Al substrate was taken out and immediately casted a mixture of epoxy resin and hardener (SY-SS-Delayed set Epoxy, USA) onto the swollen NR film. It is then cured at room temperature for 30 minutes to replicate the wrinkle patterns developed on the surface of the swollen NR film (Figure 1). By this technique swelling-induced wrinkles of NR film were successfully replicated to the surface of the cured epoxy resin.

## 4. Characterization

The equilibrium volume swelling ratio ‘Q’ of NR was calculated using the equation as follows,



**Figure 1.** Fabrication process of swelling-induced wrinkle pattern on the surface of NR film/Al substrate and the pattern replica.



**Figure 2.** (a) Optical micrograph of a typical pattern replica of an equilibrium swelled NR film, (b) diagrammatic representation of the cross-sectional view of pattern replica.

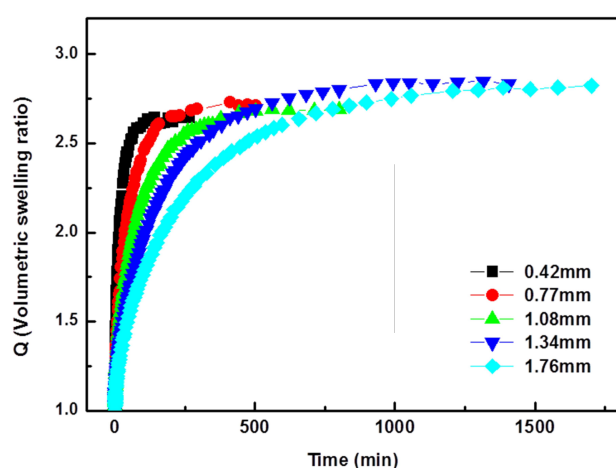
$$Q = \frac{V_r + V_s}{V_r}$$

where,  $V_r$  is the volume of NR film,  $V_s$  is the volume of the solvent absorbed by the NR film. The morphology of swelling-induced wrinkle on the surface of the swollen NR film/Al substrate was observed using an optical microscope model (ECLIPSE LV100POL Nikon, Japan). The wrinkle parameters such as the wrinkle length (L), wrinkle distance (D), wrinkle height (H) and the angle between two consecutive wrinkles ( $\theta$ ) were measured from the OM images of the pattern replica as described in Figure 2.

## Results and Discussion

### 1. Development of swelling-induced wrinkles on the surface of NR film/Al substrate

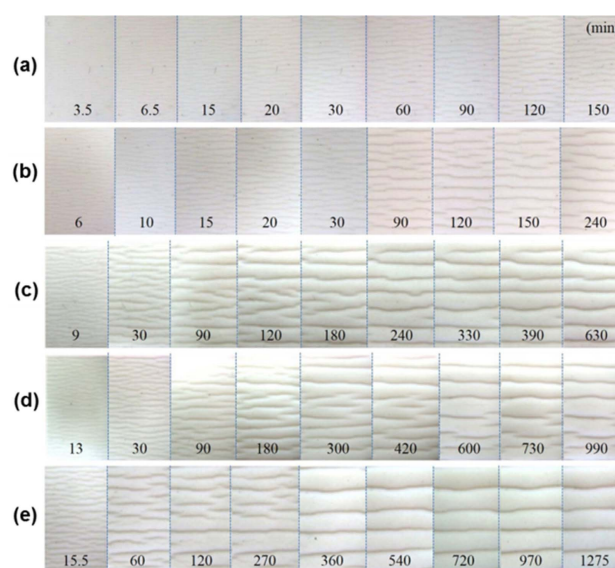
Figure 3 represents the time dependence of the swelling behavior of NR film pre-stretched and attached onto Al substrate with different thickness (0.42 to 1.76 mm). This NR film/Al substrate was swollen to an equilibrium swelling ratio in hexane. From the figure, it can be seen that the thinner NR film shows faster swelling in a short span of time. However, the thicker NR film showed a lower swelling rate, which has been confirmed from a slightly decreased slope of the swelling-time curves as the thickness of the NR film increased from 0.42 to 1.76 mm. However, the equilibrium (saturation) swelling ratio of all the NR films were almost same (about 2.63) but at a different swelling time. For instance, the saturation swelling time of the NR film with



**Figure 3.** Volumetric swelling ratios of NR film/Al substrate with different thickness as a function of swelling time.

thickness of 0.42 mm was about 250 min. For other NR films, it was about 600 min for 0.77 mm, 800 min for 1.08 mm, 1400 min for 1.34 mm and around 1700 min for 1.76 mm respectively.

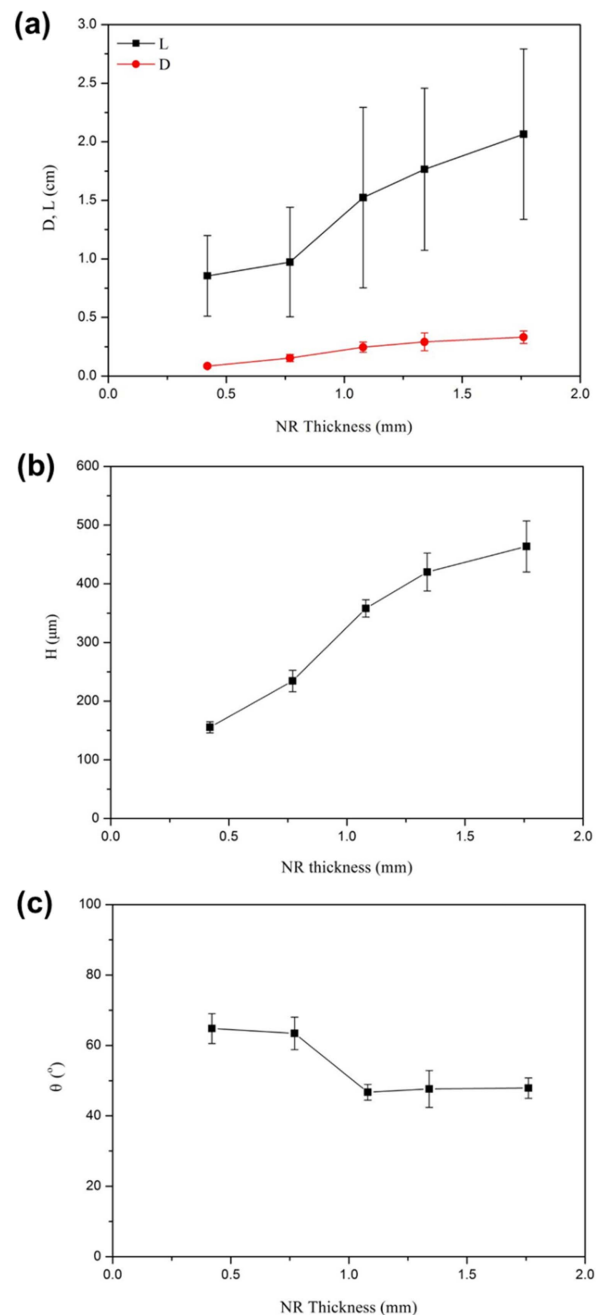
Figure 4 represents the optical photomicrographs of the swelling-induced wrinkles on the surface of NR film/Al substrate with different thickness of NR film under various swelling time. The NR film with a thickness of 0.42 mm shows some ripple patterns at the initial stages of the swelling process up to 90 min. However, certain asymmetric wrinkles were observed after a swelling time of 120 to 150 min. The wrinkling patterns observed in the NR film having thickness of 0.77 mm were almost similar to the former one. However, after 90 minutes of swelling it exhibits asymmetric wrinkles which are disconnected in certain long range. Likewise, as the thickness of NR film increased to 1.08 mm (Figure 4c) more numbers of short asymmetric wrinkles were observed on the surface even after 30 minutes of swelling. And certain continuous wrinkles were also observed after 330 minutes of swelling time. When the thickness is again increased to 1.76 mm, the more ordered and continuous wrinkling patterns were appeared identically on the surface of the NR film after 360 minutes of a swelling time as seen in Figure 4e. It is worth noting that as the thickness of the NR film increases the numbers of wrinkles decreased. However, the uniformity of the swelling-induced wrinkles was increased as the thickness increased from 0.42 to 1.76 mm.



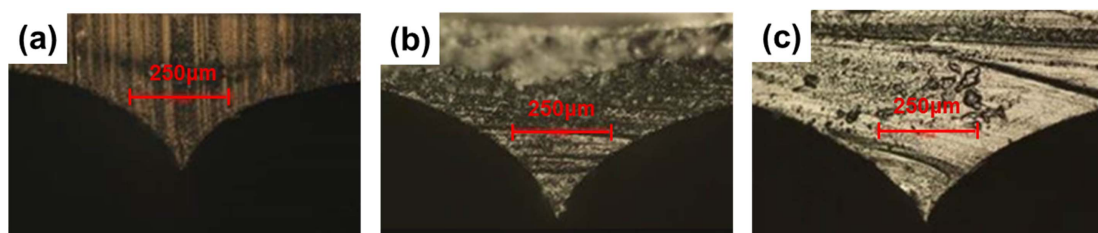
**Figure 4.** Optical photomicrographs of the swelling-induced wrinkles on the surface of NR film/Al substrate as a function of swelling time. Thickness of NR film; (a) 0.42 mm, (b) 0.77 mm, (c) 1.08 mm, (d) 1.34 mm, and (e) 1.76 mm.

## 2. Measurements of wrinkling parameters from pattern replica

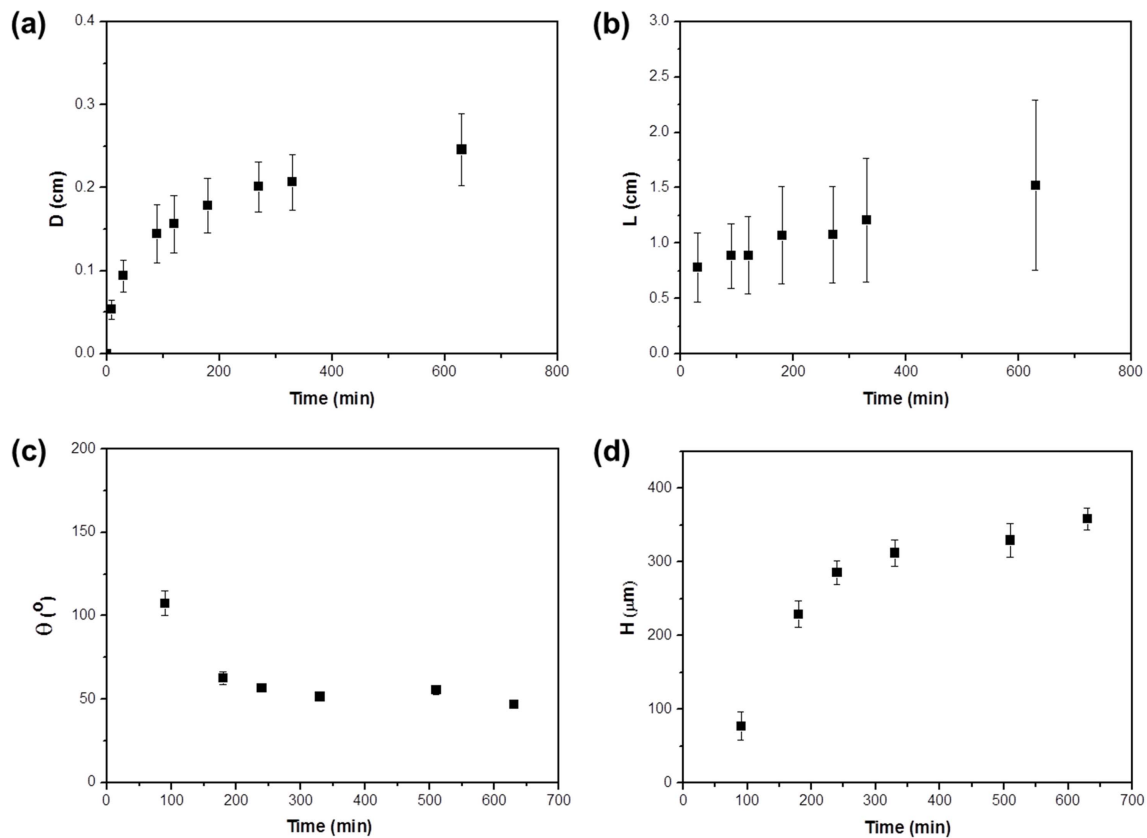
After the saturated swelling of NR film/Al substrate in hexane, we made replicas of the swelling-induced wrinkles on the surface of NR film using an epoxy-hardener system. The dimensions of the wrinkles such as the wrinkle length (L), wrinkle distance (D), wrinkle height (H) and the angle between two consecutive wrinkles ( $\theta$ ) were measured from the OM images of the cross-sections of the respective pattern replica. Figure 5a, b represent the measured values of L, D and H as a function of thickness of NR film. It can be seen from the figure that the distance (D), length (L) and height (H) of the wrinkles gradually increase as the thickness of the NR film increases. It may be possible that during the swelling of the soft elastomeric NR film/Al substrate system in hexane, the NR film undergo significant volume change which results in an anisotropic osmotic pressure along the film thickness. This osmotic pressure generates a compressive stress in the film which is released in the form of wrinkles. In the case of thin NR film, the resulted compressive force can easily wrinkle the film with low D, H and L. As the thickness of the film increases it makes difficulty in bending the film which produces fewer numbers of periodic wrinkles with high values of D, H and L as seen in Figure 4c. Unlike in the case of other wrinkling parameters, the angle ( $\theta$ ) between two consecutive wrinkles decreases as the thickness of NR film increases. Especially, a sharp reduction in  $\theta$  was noticed when the thickness increased from 0.42 to 1.08 mm, afterwards no significant change was observed in angle (Figure 5c). Figure 6 demonstrates the OM images of the cross-sections of pattern replica of the swollen NR film/Al substrate having 0.42, 1.08 and 1.76 mm thickness of NR film. It can be seen from the figure that the angle between two consecutive wrinkles is extremely sharp and it generally becomes sharper as the thickness of the film is increased from 0.42 to 1.08 mm.



**Figure 5.** Variations of swelling-induced wrinkling parameters as a function of thickness of NR film; (a) wrinkle distance, D and wrinkle length, L (b) wrinkle height, H and (c) angle between two wrinkles,  $\theta$ .



**Figure 6.** Optical photographs of the cross-sections of pattern replicas of the respective swollen NR film/Al substrate with thickness of (a) 0.42 mm (b) 1.08 mm and (c) 1.76 mm.



**Figure 7.** Variations of swelling-induced wrinkling parameters of a NR film/Al substrate with thickness of 1.08 mm; (a) Wrinkle distance, D (b) wrinkle length, L (c) wrinkle height, H and (d) angle between two wrinkles,  $\theta$ .

### 3. Effect of swelling time on the wrinkle parameters

To investigate the effect of swelling time on the various wrinkle parameters, the wrinkle formation in the NR film/Al substrate which have 1.08 mm thickness of NR film were evaluated as a function of swelling time. Figure 7 represents the variations of wrinkle parameters as a function of swelling time. The distance (D), height (H) and length (L) of the wrinkles increased as the swelling time increased. However, the angle ( $\theta$ ) measured at the initial stages of swelling was higher and subsequently decreased up to 200 minutes and thereafter it dropped slightly. It can be also explained with a compressive force of NR film induced by swelling. At the initial stages of swelling, the compressive force is small enough to make any surface deformation in the form of continuous periodic wrinkles. However, as the swelling time progress, more solvent will penetrate into the NR film, which increases the level of osmotic pressure in the film and naturally the compressive force create more sharp periodic wrinkles with higher D, H and L.

### Conclusions

The swelling-induced wrinkle was obtained from the swelling of NR film pre-stretched and fixed on an aluminum substrate in hexane. A novel pattern replication technique has been proposed to evaluate the characteristics of swelling-induced wrinkle such as the wrinkle length (L), wrinkle distance (D), wrinkle height (H) and the angle between two consecutive wrinkles ( $\theta$ ). The length (L), distance (D) and height (H) of wrinkle were increased with increasing of thickness of NR film and swelling time. However, the angle ( $\theta$ ) between two consecutive wrinkles was decreased and sharper as thickness of NR film and swelling time increased. The characteristics of swelling-induced wrinkle were successfully investigated from our replication technique using epoxy-hardener system. We believe that the proposed pattern replication methodology can help to effectively tune the surface topography to a desired level for applications requiring wrinkling patterns such as photovoltaics system, microfluidics system and stretchable electronics.

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