Submicroscopic Morphology of the Laser Induced Surface Structure of Partially Renatured Gelatin Films

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The formation of nap-type structures induced by UV-laser irradiation of renatured gelatin films with various triple helix contents was observed by an atomic force microscope. Surface topography was found to be dependent on degree of helix content (DHC), fluence, and number of applied pulses (PN). The surface roughness (R_a) increased with PN following a hyperbolic curve for the renatured gelatin films with DHC of more than ca. 7%. The increment of R_a tended to be depressed with increasing DHC.

Laser-induced surface modifications of material surfaces by the ablation technique have attracted a great deal of attention.[1–5] It is well known that laser radiation with high fluence can modify the roughness, crystallinity, resistivity, and chemical composition of polymer surfaces.[4–6] Quasiperiodic microstructures often emerge on the ablated material surface.[7–9] Furthermore, various surface structures suggested to be created by the release of tension fields induced by the laser ablation, depending on the crystallinity of polymer films.[5] Such surface modifications might improve the adhesion of polymer films to other polymer substrates.

Recently, we have investigated the formation mechanism of surface structures for collagen related biopolymers films by using an atomic force microscope (AFM) with the successive measurement technique.[10] The technique revealed that repetition of etching and shrinkage would induce the aggregation of the summits and that the thermal denaturation is responsible for the formation of the surface structure. However, the relationship between surface structures and degree of helix content (DHC) was still unclear. It is important to understand the effects of DHC on laser induced surface structure for rationalizing the generation mechanism of the structure. This paper deals with the excimer laser processing of the partially renatured gelatin films for modifying surface morphology, and the effect of the number of applied pulses (PN) on the surface roughness as a function of DHC was examined by means of AFM.

Dried collagen films used were atelocollagen film (KOKEN). Partially renatured gelatin films with various DHC were prepared by casting 2% aqueous gelatin solutions at each of the temperature of 20, 35, 40, and 60 °C, followed by the evaporation of water. When solutions of random-coil gelatin are cooled to temperatures below a critical temperature, the gelatin chain is partially transformed into the collagen chains composed of triple helices. The value of DHC refers to the regenerated triple-helix content as a function of the renaturation temperature. DHC was determined by the following equation from measuring the angle of rotation of the optical polarization[11]:

$$\mathrm{DHC} = \frac{\alpha_m - \alpha_g}{\alpha_c - \alpha_g} \times 100 \quad (1)$$

where α_m is the measured value of the angle, α_g is the value of the angle for gelatin, and α_c is the value for collagen, assumed to have 100% helix. Table 1 shows the obtained results. The laser used was an ArF (193 nm) excimer laser (LEXTRA50, Lambda Physik) whose pulse duration in FWHM was 17 ns. AFM used was Nanoscope III (Digital instruments) and operated in contact mode under atmospheric condition.

Table 1. Characteristics of partially renatured gelatin films

Sample	Cooling temp. / ℃	Helix content / %
Collagen	-	100
Helix 75	20	75±5
Helix 45	35	45±5
Helix 7	40	7±3
Gelatin	60	0

AFM images of the surfaces of samples irradiated with various PN are shown in Figure 1. The scanned area of the sample in Figure 1 is 30 × 30 μm. After irradiation with 10 pulses at 100 mJ/cm^2, the surface topography changed. The topographical change observed on the irradiated surface of the films was caused by the photothermal process of laser ablation accompanying thermal denaturation of the helical structure.[10] The degree of denaturation was estimated 40% with one shot by Fourier self-deconvolution method,[12] and then increased to 70% after 5 shots for the collagen film. The treated surface is characterized by summits and valleys. Additional laser pulses enhanced the summit–valley structure. No topographical change was observed on the irradiated surfaces of the gelatin films having no helix content. The number of the summits was decreased with increasing PN, and with increasing DHC at the same PN. The results endorsed the conclusion in the previous paper that the thermal denaturation of the helical structure was responsible for the formation of the structure.[10]

Figure 2 shows the surface roughness (R_a) plots for partially renatured gelatin films as a function of PN at 100 mJ/cm^2. The values of R_a increased with increasing DHC at a given PN. This result indicates that the surface roughness of the gelatin films induced by laser irradiation at the same PN can be controlled by changing DHC of the renatured gelatin film. The difference of the value of R_a was explained by the growing model as presented in our previous paper.[10] The number of the summits depended on the DHC. The surface roughness increased

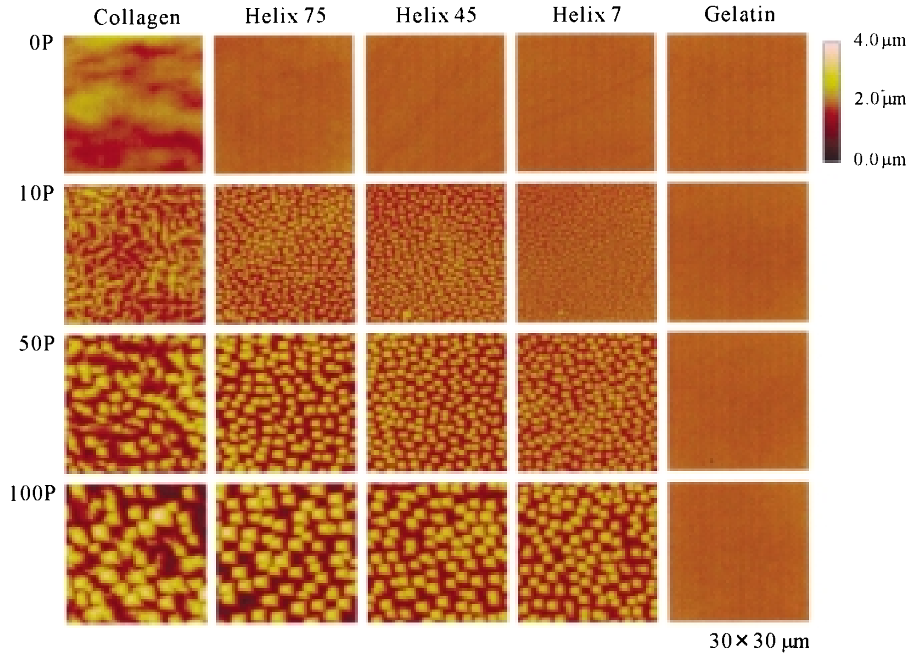

Figure 1. AFM images of partially renatured gelatin films irradiated with ArF laser at a fluence of 100 mJ/cm^2.

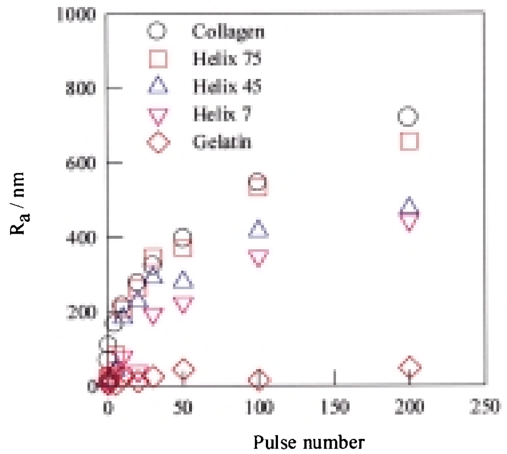

Figure 2. R_a plots for partially renatured gelatin films as a function of pulse number irradiated with ArF laser at a fluence of 100 mJ/cm^2.

with PN following a hyperbolic curve for the renatured gelatin films with DHC of more than ca. 7%. This result indicated that the helix in the film drastically changed surface topology when the film was irradiated by the laser. Interestingly, after the irradiation of 200 laser pulses, the value of R_a for the film with DHC of ca. 7% showed about 60 % of R_a for the collagen film. The surface structure is governed by an intrinsic existence of scarce triple-helices corresponding to a DHC of ca. 7% responsible for its nuclear creation. It is concluded that the surface structure would be initially generated by denaturation of the helix, however, that the aggregation of surface structures would be enhanced by repetition of etching and shrinkage.

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