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ORIGINAL ARTICLE

Application of the UV laser printing technique to soft gelatin capsules containing titanium dioxide in the shells

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Abstract
Aim: The purpose of this study was to examine application of ultraviolet (UV) laser irradiation to printing soft gelatin capsules containing titanium dioxide (TiO_2) in the shells and to study effect of UV laser power on the color strength of printing on the soft gelatin capsules.

Methods: Size 6 Oval type soft gelatin capsules of which shells contained 0.685% TiO_2 and 0.005% ferric dioxide were used in this study. The capsules were irradiated pulsed UV laser at a wavelength 355 nm. The color strength of the printed capsules was determined by a spectrophotometer as total color difference (dE).

Results: The soft gelatin capsules which contained TiO_2 in the shells could be printed gray by the laser. Many black particles, which were associated with the printing, were formed at the colored parts of the shells. It was found that there were two inflection points in relationship between output laser energy of a pulse and dE. Below the lower point, the capsules were not printed. From the lower point to the upper point, the capsules were printed gray and total color difference of the printing increased linearly in proportion with the output laser energy. Beyond the upper point, total color difference showed saturation because of micro-bubbles formation at the laser irradiated spot.

Conclusions: Soft gelatin capsules containing TiO_2 in the shells could be performed stable printing using the UV laser printing technique. Color strength of the printing could be controlled by regulating the laser energy between the two inflection points.

Keywords: Printing, soft gelatin capsules, color strength, UV laser, titanium dioxide, total color difference (dE), output laser energy

Introduction

Method and identification system to keep track of individual medicines dispensed to patients in a hospital is important to avoid severe health risks[1–3]. Medicines come in a variety of shapes, sizes and colors to help distinguish one from the other. However, there is a restriction in keeping good identification characteristics only with the differences in size, shape, color of tablets or capsules so that marking directly on the medicines become more important for identification method. The offset printing, ink-jet printing, and pad printing are the popular methods to print marks on the surface of medicines using an ink. But manufacturing troubles, such as illegibility, blur or dirt of printing are easy to be induced by the surface roughness of the medicines, environmental conditions of process room so that it is necessary to control strictly both the viscosity, uniformity, temperature and drying of the ink to obtain clear printing during manufacturing.

In case of film-coated tablets containing titanium dioxide (TiO_2) in the films, we reported about development[4], characteristics, and printing mechanism[5,6] of an ultraviolet (UV) laser marking device, which imprints on the surface of film-coated tablets by irradiation of UV laser at a wavelength 355 nm. When the UV laser was irradiated to the film, many amounts of black particles, which were agglomerates of grayed oxygen defected TiO_2 formed by the UV laser irradiation, were formed in the irradiated spots of the film and the spots showed their color change from white to gray. Titanium dioxide in the film played an important role for the printing film-coated

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tablets by the UV laser. The color strength of the printing film was not changed by particle size, crystal structure, and concentration of TiO_2 in the film, but could be controlled by regulating the irradiated UV laser power.

A soft gelatin capsule is a one-piece, hermetically sealed soft gelatin shell containing a solution, a suspension, or a semisolid and is one of unique pharmaceutical oral dosage forms. Gullapalli reported a review[7] that soft gelatin capsules enable improvement of poorly soluble compound absorption, masking odors and unpleasant taste, and protecting the encapsulated compound against oxygen and light. There are three kinds of typical shapes, Round, Oval, and Oblong in soft gelatin capsules. In all cases of the soft gelatin capsules, the printing area is not flat but rounded so that it is difficult to do printing soft gelatin capsules using an ink. Yoshino[8] reported about the development of printing device to soft gelatin capsules using a CO_2 laser. When the CO_2 laser was irradiated to the soft gelatin capsules, gelatin, one of the constituents of soft gelatin capsule shell was denatured by heat of the CO_2 laser, and the irradiated whitened spots led to the printing. The printing was performed without touching objects so that there were no problems such as blur or dirt of the printing induced by an ink. However, in case of white or light colored soft gelatin capsules, the printing could not be applied because of lack of legibility and it has been hoped development of new printing technologies for the soft gelatin capsules.

The purpose of this study was to try an application of the UV laser printing technique as one of methods to perform legible printing on white or light colored soft gelatin capsules containing TiO_2 in the shells and to clarify how color strength of printing on the soft gelatin capsules could be controlled by the irradiated laser power.

Materials and methods

Materials

Commercially available soft gelatin capsules used in this study were size 6 Oval type prepared by a rotary die process[9,10]. The filled content weight and the shell weight of the capsule were 325 mg and 200 mg, respectively. The shells contained 0.685% TiO_2 and 0.005% Ferric dioxide and looked ivory white. The TiO_2 was anatase type and BET diameter was 177.2 nm.

UV laser irradiation

A tripled Nd:YVO4 laser (DS20H-355, Photonics Industries International, INC, NY), producing pulsed laser of up to 8 W peak pulse power by AO-Q switch was used for UV laser irradiation. The pulse repetition rate of the laser was 10, 20, or 30 kHz, respectively. The laser was set to a wavelength 355 nm and diameter of the laser spot was 0.1 mm. Square areas (8.0 mm × 4.7 mm) of the capsules were irradiated the pulsed UV laser by scanning at a speed of 2000, 4000 or 6000 mm/s for the pulsed laser of 10, 20 or 30 kHz pulse repetition rate, respectively by parallel with 0.05 mm distance lattice controlled by CAD system so as to control numbers of the pulsed spots per the printed area same in all experimental conditions (Figure 1 shows an example of the printed soft gelatin capsule.).

Total color difference (dE)

Color strength of the printings of soft gelatin capsules was examined by a spectrophotometer (SE-2000, NIPPON DENSHOKU Co. Ltd., Tokyo, Japan) using a non-printed capsules as a reference. This enables examination of the L*a*b* co-ordinate which closely represents human sensitivity to color[11]. Equal distances in this system equal perceived color differences where L* is the lightness variable while a* (green to red) and b* (blue to yellow) are chromaticity co-ordinates. The color strength of the printed capsules was estimated by a spectrophotometer as total color difference (dE), which is a straight-line distance between co-ordinates of the printed area of soft gelatin capsule and the non-printed capsule, and is calculated using Equation (1).

$$dE = [(dL^*)^2 + (da^*)^2 + (db^*)^2]^{1/2} \quad (1)$$

Results and discussion

Printing soft gelatin capsules by the UV laser irradiation

In previous papers, we reported about development of a UV laser printing machine[4], which imprinted on the surface of film-coated tablets by irradiation of UV laser at a wavelength 355 nm and the printing mechanism[5]. Titanium dioxide in the film played an important role for the printing film-coated tablets by the UV laser. Titanium dioxide is often contained in the shells of soft gelatin capsules as an opacifier[7,12] so that it was assumed that even the ivory white soft gelatin capsules also could be printed gray by the UV laser irradiation. In this study, we examined application of the UV laser printing technique[4–6] to ivory white soft gelatin capsules containing TiO_2 in the shells.

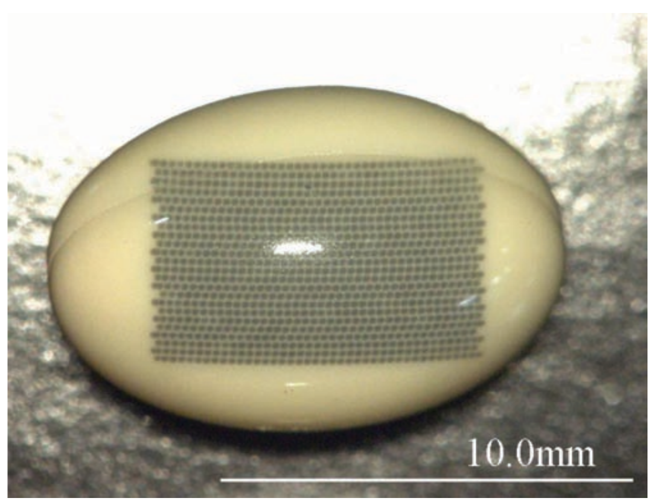

Figure 1. A photograph of a soft gelatin capsule irradiated the 5.05 W, 20 kHz pulsed UV laser. The area irradiated the pulsed UV laser showed its color change from ivory white to grayed spots.

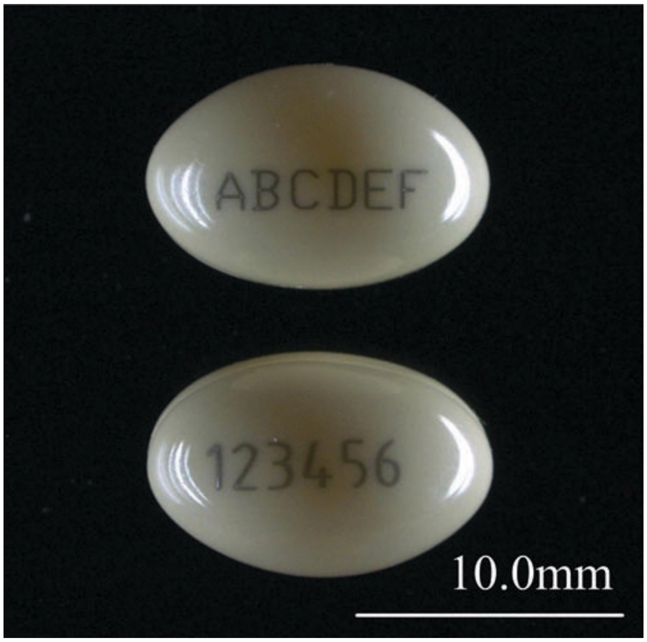

Figure 2. Representative photographs of soft gelatin capsules printed by the UV laser printing technique.

Figure 1 shows a photograph of color change of a soft gelatin capsule containing TiO_2 in the shell when it was irradiated 5.05 W, 20 kHz UV laser at wavelength 355 nm. The area of the capsule shell where the UV laser was irradiated showed a visible change in its color from ivory white to gray. Recently, a CO_2 laser is used as one of methods[13] for marking pharmaceutical dosage units and Yoshino[8] reported about development of a printing device to soft gelatin capsules using the CO_2 laser. When the CO_2 laser was irradiated to the soft gelatin capsules, gelatin, one of the constituents of soft gelatin capsule shells was denatured by heat of the CO_2 laser, and the heat-formed whitened spots led to the printing on the soft gelatin capsules. So, in case of white or light colored soft gelatin capsules, the printing could not be applied because of lack of color differences between the medicines and the whitened spots. Figure 2 shows a representative photograph of the soft gelatin capsules printed with the UV laser irradiation technique[4]. In this study, it was found that even if the soft gelatin capsules were white or light colored and could not be done printing by the CO_2 laser, the capsules containing TiO_2 in the shells were able to be performed printing gray by the UV laser irradiation like the film-coated tablets reported previously[5,6].

Figure 3 shows photographs of the colored parts of the shells irradiated 5.05 W, 20 kHz UV laser by a Zoom Stereo Microscope (VHX-900, Keyence Co., Ltd., Osaka, Japan). Figure 3-(A) is a photograph (×1000) taken from the surface of the printed shell and Figure 3-(B) is a photograph (×200) of a cross section of the shell. A diameter of the laser spot was 0.5mm and all of the spot area where the UV laser was irradiated was not grayed uniformly, but many amounts of black particles were observed at the colored part of the shell. These are similar results with the film-coated tablets[5]. The shells of the soft gelatin capsules used in this study were 541.6 ± 17.0 µm (mean ± SD $n = 5$) thickness. A diameter of the black particles was about 1µm and the particles were observed at the area from the surface to 69.16 ± 8.27 µm (mean ± SD $n = 5$) depth of the shells. In case of printings using inks, the printings were performed only on the surfaces of medicines. The inks were sometimes rubbed off and cosmetic problems such as mottled appearance, blur, or dirt of the inks were happened in case of soft gelatin capsules. When the UV laser was used for printing soft gelatin capsules, not only the irradiated surfaces of the capsule shells but also the insides were printed as shown in Figure 3-(B) so that the printing by the UV laser printing technique was very stable against frictions.

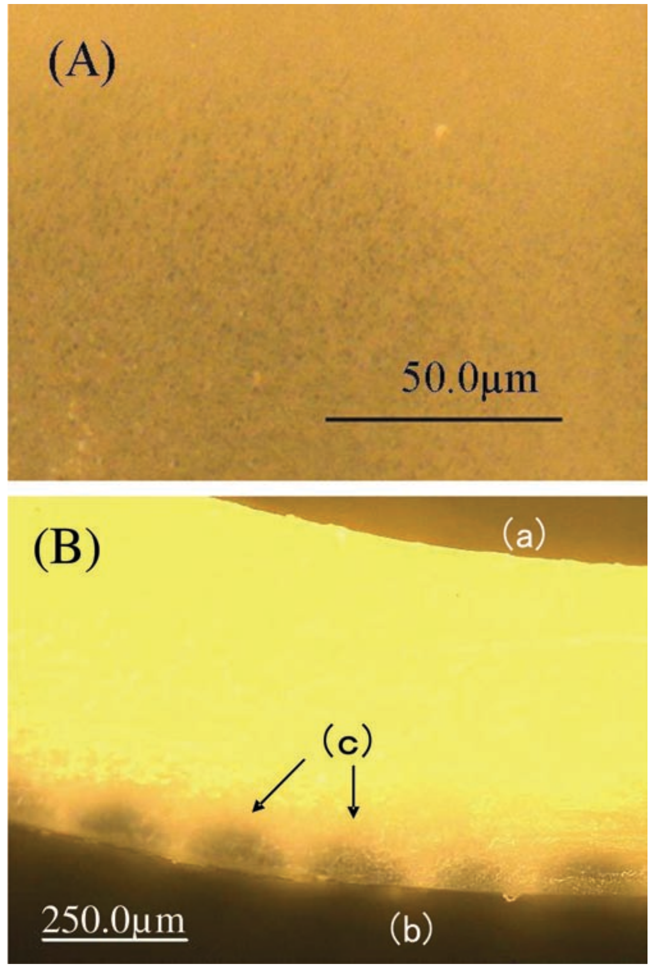

Figure 3. Photographs of the colored parts of the shells irradiated the UV laser. (A) is a photograph (×1000) taken from surface of the shell and (B) is a one (×200) of the cross section of the shell. Symbols (a) and (b) are inside and outside of the soft gelatin capsule shell, respectively. The black areas (c) in the shell in photograph-(B) are the spots irradiated the pulsed UV laser.

The soft gelatin capsules were able to be performed printing gray by the UV laser irradiation like the film-coated tablets. It was found that all of the area where the UV laser was irradiated was not grayed uniformly, but many amounts of black particles were observed at the colored parts of the shells and these black particles were associated with the printing. The printing on the soft gelatin capsules by the UV laser was stable under 40/75% up to 6 months or illumination of light by xenon lamp up to 1.2×10^6 l x·hour (data not shown). These findings were in good agreements with the results reported previously[6] about the printing film-coated tablets.

Effect of UV laser energy on color strength of the printing soft gelatin capsules

In case of film-coated tablets[6], there was only one inflection point (1.6 W) in relationship between the irradiated UV laser power and dE. When the irradiated UV laser power was below the point, the film was not printed. Beyond the point, grayed printing was performed, and total color difference of the printing increased linearly in proportion with the irradiated laser power. Black particles which were agglomerates of the oxygen defected grayed TiO_2 were associated with the printing. The inflection point was a minimal energy to form the agglomeration of the oxygen defected grayed TiO_2. The color strength of the printed film was not changed by particle size, crystal structure, and concentration of TiO_2 in the film but could be controlled by regulating the irradiated UV laser power beyond the inflection point. So in this study, we focused on the UV laser power as a regulating factor of UV laser printing, and examined effect of the UV laser power on the color strength of printing on the soft gelatin capsules.

Figure 4 shows the relationship between the irradiated UV laser power at pulse repetition rate, 10 kHz (closed triangle), 20 kHz (open circle), or 30 kHz (closed square) of the pulsed laser and dE of the printing on the soft gelatin capsules. In case of the pulse repetition rate of 10 kHz, total color difference increased linearly in proportion with the irradiated UV laser power up to 2 W, and beyond 2 W, it became plateau and gradually decreased up to 6 W. In case of the pulse repetition rate of 20 kHz, when irradiated power was below 0.8 W, total color difference was zero and the capsules were not printed. From 0.8 W to 4 W, total color difference increased linearly in proportion with the irradiated UV laser power and showed saturation beyond 4 W. In case of the pulse repetition rate of 30 kHz, below 1.5 W, total color difference was zero, and the capsules were not printed. From 1.5 W to 6.5 W, total color difference increased linearly in proportion with the irradiated UV laser power, and showed saturation beyond 6.5 W. In case of film-coated tablets[6], there was only one inflection point in relationship between the irradiated UV laser power and dE, and when the power was beyond the point, total color difference increased linearly in proportion with the irradiated power. On the other hand in case of soft gelatin capsules, there were one or two inflection points. It was found that the relationship between output laser power and dE was greatly affected by the pulse repetition rates.

In case of the pulsed laser used in this study, the output laser power (W) is converted to the output laser energy (J) of a pulse by Equation 2.

$$E = P/R \qquad (2)$$

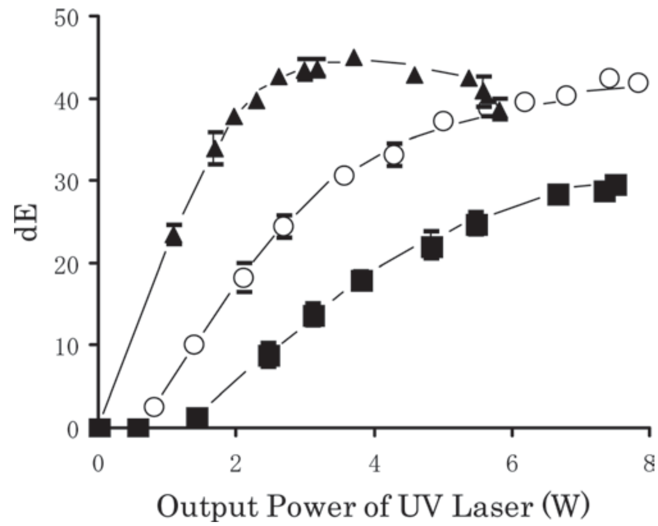

Figure 4. Relationship between output power of UV laser and dE of printed soft gelatin capsules. The pulse repetition rates of the pulsed laser were 10 kHz (closed triangle), 20 kHz (open circle) and 30 kHz (closed square). Each point represents mean ± SD ($n = 3$).

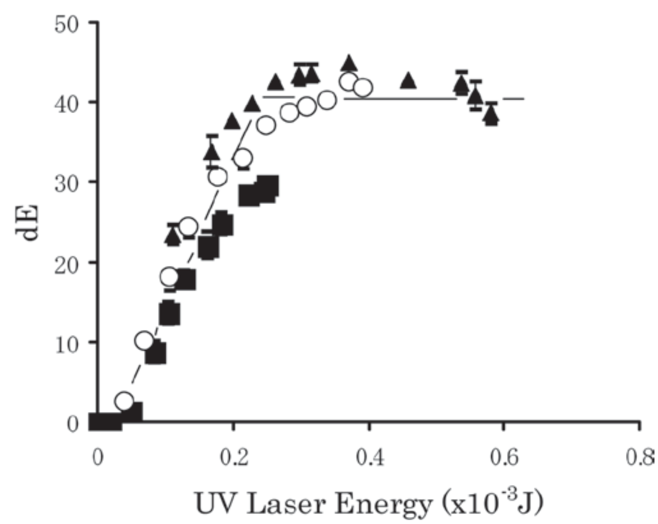

Figure 5. Relationship between output UV laser energy and dE of printed soft gelatin capsules. The pulse repetition rates of the pulsed laser were 10 kHz (closed triangle), 20 kHz (open circle) and 30 kHz (closed square). Each point represents mean ± SD ($n = 3$).

Where, E, P and R are output laser energy (J) of a pulse, output laser power (W) and pulse repetition rate (Hz) of pulsed laser, respectively.

Figure 5 shows the relationship between the output laser energy of a pulse and dE by modifying Figure 4. By using the output laser energy parameter instead of the output laser power, color strength of the printing soft gelatin capsules by the UV laser could be standardized and estimated systematically independent of the pulse repetition rates as shown in Figure 5. It was clearly found that there were two inflection points (0.05×10^{-3} J/pulse and 0.25×10^{-3} J/pulse) in relationship between the output laser energy of a pulse and dE. There existed

3 phases. Below the lower infliction point (0.05×10^{-3} J/pulse), total color difference of the printing was nearly zero (first phase). The capsules were not printed and looked ivory white. From the lower point to the upper inflection point (0.25×10^{-3} J/pulse), the capsules were printed gray and total color difference increased linearly in proportion with the output laser energy of a pulse (second phase), and beyond the upper point, total color difference showed saturation (third phase). Color strength of the printing soft gelatin capsules could be controlled by regulating the UV laser energy between the two inflection points. As reported previously[6], the lower point was a minimal laser energy to form the agglomeration of the grayed oxygen defected TiO_2 to the black particles so that the minimal laser energy for the soft gelatin capsules (0.05×10^{-3} J/pulse) was close to one for the film-coated tablets (0.08×10^{-3} J/pulse). On the other hand, the upper inflection point observed in this study was not observed in case of the film-coated tablets[6].

Morphological observation of the UV laser irradiated spots

Figure 6 shows photographs (×1000) of the spots irradiated each level of the output UV laser energy (0.04×10^{-3} J/pulse, 0.13×10^{-3} J/pulse, 0.25×10^{-3} J/pulse, 0.28×10^{-3} J/pulse, or 0.39×10^{-3} J/pulse) by the Zoom Stereo Microscope. At the first phase (0.04×10^{-3} J/pulse), the capsules were not printed and the formation of the black particles was observed little. At the second phase (0.13×10^{-3} J/pulse, and 0.25×10^{-3} J/pulse), it was confirmed that many numbers of black particles which were associated with the printing shells, were formed in the UV laser irradiated spots.

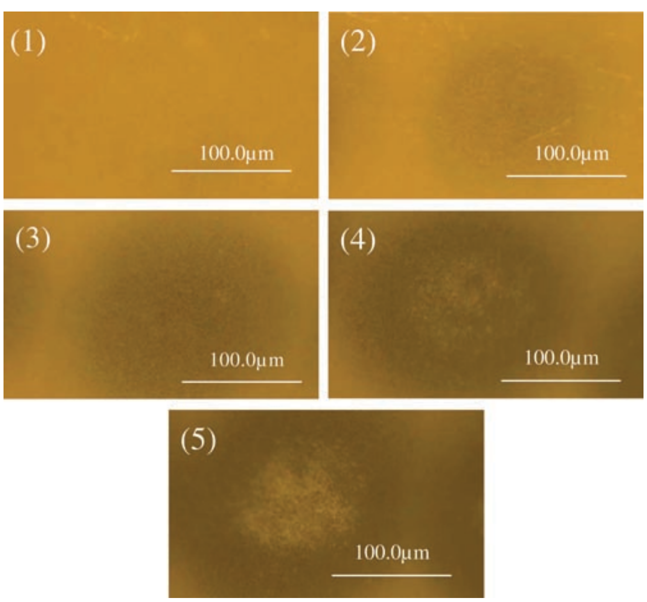

Figure 6. Photographs (×1000) of spots irradiated each of UV energy by zoom stereo microscope. The irradiated UV laser energy was (1); 0.04×10^{-3} J/pulse, (2); 0.13×10^{-3} J/pulse, (3); 0.25×10^{-3} J/pulse, (4); 0.28×10^{-3} J/pulse, or (5); 0.39×10^{-3} J/pulse, respectively.

The higher the irradiated UV laser power became, the more the number of black particles formed in the spots became. This shows that the lower point was a minimum energy to form the black particles in the shells like the case of film-coated tablets. At the third phase (0.28×10^{-3} J/pulse, and 0.39×10^{-3} J/pulse), it was morphologically observed that many micro-bubbles were formed in the irradiated spots in addition to the black particles. The higher the irradiated UV laser energy became, the more the micro-bubbles were formed in the spots. The micro-bubbles formed in the spots dispersed light so that the spots became white. The upper inflection point was minimal laser energy to form the micro-bubbles in the gelatin shells. As the irradiated UV laser energy increased beyond the upper inflection point, the agglomeration of the grayed oxygen defected TiO_2 to the black particles increased. But at the same time, the formation of the micro-bubbles increased so that total color difference showed the saturation and was constant at the third phase.

Lazare et al[14]. reported for the first time that micro-foam was formed in biopolymer films, for example collagen and chitosan, containing ~15% water, by a KrF laser irradiation, of which wavelength was 248 nm. The foaming required a sudden and dense bubble nucleation and growth by acoustic wave induced by the laser pulse. They concluded that the water content of the films was important because it provided the tensile weakness necessary for bubble nucleation and growth with evaporation induced by the laser irradiation leading to the expansion of the whole material that yielded the micro-foam. There are some reports that similar micro-foam was formed in gelatin film by UV laser irradiation. Gaspard et al.[15,16] reported that laser irradiation with UV at 248, 266, and 355 nm ns pulses induced dramatic structural changes in the irradiated gelatin films in the form of a foaming layer with nanometric size pores and bubbles. Oujja et al[17]. also reported that UV laser irradiation of gelatin films induced dramatic structural changes in the irradiated films and discussed that high water content of gelatin films reduced the tensile strength of the biopolymer and facilitated bubble nucleation and growth together with an eventual expansion of the material in a micro-foam layer. Recently, Lazare et al.[18,19] theoretically reported that polyvinyl acetate, polymer allowed discussing the role of the viscosity drop in the dynamics of the laser-induced cavitation by model of pressure or thermoelastic wave induced by the absorption of the laser pulse. The polymer studied has high viscosities typical of solids at room temperature and can be transiently liquefied upon pulse laser heating in the usual laser ablation conditions. By using only one laser pulse which provides enough heating to produce the tensile wave and reduce the viscosity to reach the viscosity of a liquid, a foaming transition of the polymer surface can be obtained by a mechanism of cavitation and bubble growth. The negative pressure of the polymer provides the cavity expansion. The ablation gas can diffuse into the expanded cavity and equilibrate the outer ambient pressure when the tension pulse is over. The inner remaining gas pressure at the end of the tension pulse has the role of equilibration and stability of the final micro-bubbles. The phenomenon of laser-induced forming is strongly dependent on the polymer viscosity by means of the dependence of the parameter on the temperature and pressure. The micro-bubbles found at the third phase in this study might be formed by the same mechanism. The shells of soft gelatin capsules generally contain ~30% plasticizer[7] and about 10% water, and are plastic. So, the bubbles might be formed easily in the shells when the shells were irradiated the pulsed UV laser at more over 0.25×10^{-3} J/pulse. In previous report[6] about hydroxypropylmethylcellulose (HPMC) film of film-coated tablets, we reported that there found one inflection point in relationship between output laser power and dE. Color strength of the printing by the UV laser irradiation could be controlled by regulating the UV laser power beyond the inflection point. The upper inflection point observed in case of the soft gelatin capsules in this study could not be observed up to 0.35×10^{-3} J/pulse irradiation[6] in case of the HPMC films of film-coated tablets because of upper limit of UV laser power, and might be bigger than 0.35×10^{-3} J/pulse.

When the UV laser technique was applied to the printing, there existed two inflection points in relationship between output laser energy and dE. The lower point was a minimal laser energy to form the agglomeration of the oxygen defected TiO_2 to the black particles which were associated with the printing. The upper point was minimal laser energy to form micro-bubbles in the shells or films. Color strength of the printing by UV laser could be controlled by regulating the laser energy between the two points.

Conclusions

Soft gelatin capsules which contained TiO_2 in the shells could be printed gray by the UV laser. In relationship between output laser energy of a pulse and dE, there were two inflection points. There existed 3 phases. Below the lower point (0.05×10^{-3} J/pulse), the capsules were not printed. From the lower point to the upper point (0.25×10^{-3} J/pulse), the capsules were printed gray and total color difference of the printing increased linearly in proportion with the output laser energy. Color strength of the printing could be controlled by regulating the UV laser energy between the two inflection points. Beyond the upper point, total color difference showed saturation because of the micro-bubble formation at the UV laser irradiated spot.

Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this paper.

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