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Microhole Formation Behavior of Polypropylene Film Using CO₂ Laser Irradiation

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Abstract: Biaxially oriented polypropylene films produced by simultaneous equi-biaxial stretching to the draw ratio of 4×4 were perforated by the carbon dioxide laser under various laser fluences up to 426.3 J/cm². After applying various laser fluences, the irradiated area was observed using a laser scanning confocal microscope. With the increase of fluence, the surface deformation with the formation of a crater surrounded by a doughnut-like rim was firstly observed at the laser fluence of 49.7 J/cm², followed by the starting of the formation of a microhole surrounded by the rim at 113.7 J/cm². The diameter of the microhole and the size of the rim increased rapidly with the increase of laser fluence. Mechanisms for the formation of a crater, the opening of a microhole, and the formation of surrounding rim were considered to be related to the surface tension and the shrinkage caused by molecular orientation relaxation. On the other hand, volume loss from the laser irradiated area was negligibly small at the moment of microhole opening, and started to increase rapidly when the fluence reached around 150 J/cm². The microhole formation behavior was also observed by a high-speed camera. The velocity of microhole opening increased rapidly at first, presumably during the laser irradiation, and then slowed down after the cessation of laser irradiation. Theoretically estimated temperature distribution along the film thickness was compared with the laser perforation behavior. Starting of the deformation of film matched well with the starting of melting of the film surface. Film temperature was lower than the thermal decomposition temperature at the moment of the opening of a microhole, whereas at the moment of the starting of volume loss, film temperature was lower than the decomposition temperature estimated based on the heating rate of laser irradiated area, indicating that the decomposition and vaporization continues for a while after the cessation of laser irradiation.

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Introduction

In recent years, application of laser processing in the field of polymer processing has been expanding. One of the applications is in the food packaging industry. Laser perforating technology, i.e. formation of tiny holes on the films, plays an important role, especially in the fabrication of packaging for fresh fruits and vegetables. The films with high gas permeability have the ability to create a modified atmosphere inside the packages because this film

allows respiratory gases of fruits and vegetables to flow in and out of the package through the microholes, resulting in a retardation of biological processes. This can help to maintain the freshness of fruits and vegetables [1–4].

Laser technology for providing microholes on the plastic films offers numerous advantages such as higher preciseness, faster processing time, and contactlessness over traditional mechanical techniques such as hot needle and cold needle punching [5, 6]. Laser process is used to make tiny

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holes consistently on polymer films at the speed applicable to commercial production lines. The diameters of perforated microhole are normally in the range of 40–250 μm [2, 7].

Other key requirements for the food packaging films are optical transparency and mechanical properties. Polypropylene is an attractive candidate for packaging applications because of its low cost and good thermal stability [8]. Moreover, through the biaxial stretching process, mechanical properties and transparency can be improved along with the development of molecular orientation [9]. Therefore, the biaxially oriented polypropylene (BOPP) films have drawn attention for use as a microperforated film [10]. Biaxially oriented films are normally produced through the sequential biaxial stretching process, in that the unoriented starting sheet is firstly stretched uniaxially along the machine direction using a set of rollers and then stretched in the transverse direction using a tentering machine. Recently, a novel film processing equipment for the simultaneous biaxial stretching process utilizing a linear-motor system was developed. This technique allows the commercial production of uniform and highly oriented films at high speeds, while minimizing the energy consumption based on the nature of one-step-biaxial-stretching. Moreover, a laboratory-scale batch type biaxial stretching device, which can simulate closely the stretching conditions of the above mentioned novel film stretching system, has been developed [9, 11]. In this research, BOPP films were prepared using the batch-type film stretching device stated above.

Even though only a few papers reported the microhole formation on plastic films, there also are several studies in the literature addressing the laser ablation behavior on polymer surface. Among various kinds of laser, the CO_2 laser with the wavelength of 10.6 μm is most commonly used for the processing of polymers. The CO_2 laser is generally well-absorbed by common non-metal materials. The photon energy of CO_2 laser is much lower than the energies of chemical bonds in polymer materials. Thus, thermal process based on energy absorption, volumetric heating, melting, decomposition and vaporization might be the dominant processes for the laser ablation and material removal [6, 12–14]. The polymer materials also could be cut by laser [6, 15]. It was also reported that polymers are decomposed producing the volatile products using high laser fluences [16]. The processing and material parameters are also reported

to play an essential role for the quality of the microholes [15, 17, 18].

However, very few studies reported the behavior of microhole formation through the irradiation of CO_2 laser on the polymer film. Therefore, the objective of this research was set to study the effect of laser fluence on the time-course opening of microhole on BOPP films. Volume loss after the laser perforation were also evaluated.

Experimental

Materials

Polypropylene (PP) supplied by HMC Polymers Co. Ltd., Thailand was used in this study. The melt flow index and the melting temperature (T_m) of the polymer were 3 g/10 min (190 $^{\circ}\text{C}$, 2.16 kgf) and 165 $^{\circ}\text{C}$, respectively.

Films preparation

The unoriented PP sheets with a thickness of approximately 330 μm were prepared using a laboratory-scale flat die film line (Dr. COLLIN GmbH, GERMANY) equipped with a 20 mm diameter single screw extruder with the L/D ratio of 25, a mixing section of 2.5 D at the end, and a compression ratio of 3:1. A T-die with the width of 200 mm and the die gap of 0.3 mm was attached to the extruder. Barrel (zones 1–4), adapter (zone 5) and die temperatures (zone 6–7) were set to 40, 180, 190, 210, 210, 215 and 215 $^{\circ}\text{C}$, respectively.

The PP sheet extruded at a moderate screw speed of 72 rpm with the resultant through-put rate of 60 g/min was subsequently quenched on a water circulated chill roll with controlled temperature of 90 $^{\circ}\text{C}$. The take-up speed of the chill roll was kept at a relatively low speed of 1.0 m/min in order to minimize the molecular orientation development in the as-cast sheets.

Square films of 75 $\times$ 75 mm were cut from the prepared as-cast PP sheet aligning each side in the machine direction (MD) and the transverse direction (TD) of the as-cast sheet, respectively. The precursor films were biaxially stretched in a simultaneous mode using a lab scale stretcher (Karo IV, Bruckner, GERMANY). In this process, the PP films were preheated at 150 $^{\circ}\text{C}$ for 40 s and stretched at a temperature of 150 $^{\circ}\text{C}$ with the stretching ratios in MD and TD ($\lambda_{\text{MD}} \times \lambda_{\text{TD}}$) of 4 $\times$ 4. The stretching strain rates in MD and TD were fixed at 400 %/s. The obtained biaxially oriented PP (BOPP) films were

subjected to the laser perforation experiments.

Differential Scanning Calorimetry (DSC)

Thermal properties of the BOPP films were investigated using a differential scanning calorimetry, DSC (Q100, TA Instruments, USA). Samples of about 5 mg were tested under nitrogen gas flow with a heating rate of 10°C/min. Crystallinity of the film was estimated from the endothermic heat of melting assuming the heat of melting for the 100 % crystallinity of 209 J/g [19].

Birefringence

Birefringence measurement is the optical technique for analysing molecular orientation in anisotropic samples by measuring the retardation of polarized light passing through the sample with optical anisotropy. The birefringence of the stretched films was measured using a polarizing microscope (BX 53, Olympus, JAPAN) equipped with two pieces of polarizers which are set in the upside and downside of the microscope stage respectively. The optical retardations of the sample were evaluated from the normal direction (ND) to the film surface and the direction with the tilting angle of φ in the MD-ND plane using a Berek compensator. The birefringence values were calculated following the Stein's equations [20] as following:

$$\Delta n_{MD-TD} = \frac{\lambda_0 R_0}{d_0} \quad (1)$$

$$\Delta n_{MD-ND} = \frac{\lambda_0}{d_0} \left[\frac{R_0 - R_\varphi (1 - \sin^2 \varphi / n^2)^{1/2}}{\sin^2 \varphi / n^2} \right] \quad (2)$$

$$n = \frac{n_{MD} + n_{TD} + n_{ND}}{3} \quad (3)$$

$$\Delta n_{TD-ND} = \Delta n_{MD-ND} - \Delta n_{MD-TD} \quad (4)$$

where Δn_{MD-TD} , Δn_{TD-ND} , Δn_{MD-ND} are the refractive index difference (birefringence) between indicated two axes, λ_0 and d_0 are the wavelength of the incident light and the film thickness, respectively. R_0 and R_φ are the retardations with the tilting angles of 0 and φ expressed in units of number of waves, and n represents the average refractive index of the PP, which is 1.49 [19].

Thermal shrinkage

Thermal shrinkage of the film was measured following the ASTM D 2732. The BOPP films were cut as squares of 3 × 3 cm on sides in MD and TD. Shrinkage percentage in MD and TD was determined by measuring the size of the PP film sample after immersion in an oil-bath of 145 °C for 10 s. The

following equation was used for the calculation of percent shrinkage:

$$Shrinkage (\%) = \frac{L_{initial} - L_{final}}{L_{initial}} \times 100 \quad (5)$$

where $L_{initial}$ and L_{final} are the lengths of the sample before and after immersion in the oil bath, respectively.

Thermo-gravimetric Analysis (TGA)

The thermo-gravimetric analysis, TGA, is widely accepted as a standard method to investigate the thermal degradation of polymer materials. The decomposition temperature (T_d) of the BOPP film was analyzed by a TGA (TGA/SDTA 851 e, Mettler Toledo AG, Canada). The tests were carried out from ambient temperature (25 °C) to 800 °C in a nitrogen atmosphere with a flow rate of 60 ml/min. Three heating rates of 10, 100 and 200 K/min were adopted. At the heating rate of 10 K/min, the heat of decomposition was also evaluated. It should be noted that the obtained exothermic heat included the effect of endothermic heat needed for vaporization of the decomposed material.

Laser perforation

The BOPP films were perforated using a CO₂ laser (Ti60, Synrad, USA) with the power of 60 W and the wavelength of 10.6 μm. A schematic of the laser perforation system with the CO₂ laser source, a mirror and a lens is shown in Fig. 1. In the perforation process, a laser beam emitted from the laser source was reflected by a mirror at an angle of 90°, passed through a focusing lens with a focal length of 38.1 mm and then irradiated on the film surface. The focal spot diameter was approximately 103 μm. A single-shot laser pulse with the fluences of 14.2 to 426.3 J/cm², which correspond to the pulse durations of 10 to 300 μs, were applied for making a microhole. The laser beam has the Gaussian intensity distribution, and the value of fluence corresponds to the peak value at the center of the laser beam on the film.

Optical Microscope

The images of the microhole were observed by an optical microscope, OM (BH2, Olympus, JAPAN) at the magnification of 200×. Images captured and stored as grey-scale digital files of 4000 × 3000 pixels were used for measuring the sizes of the microholes in MD and TD.

Scanning Electron Microscope

The images of the microhole were also observed using a scanning electron microscope (SEM, SM-2000,

Topcon, JAPAN). The top view and the view for the cross-section of the area of laser irradiation were prepared.

3D Laser Scanning Confocal Microscope

Surface profile of the films after laser irradiation was examined using a laser scanning confocal microscope (VK-X200, Keyence, JAPAN). From the generated high-resolution images detailed profiles as well as amount of volume loss were analysed.

In-situ Observation of microhole opening

For the in-situ observation of the microhole opening behavior, a high-speed camera (Phantom V 9.0, Vision Research, Inc.) equipped with a bellows focusing attachment (PB-6, Nikon Corp., JAPAN) and a lens of 105 mm, f/2.8 (Nikon AF Micro, Nikon Corp., JAPAN) was used in this study. The light source was a 450 W metal halide lamp. The images were recorded at a frame rate of 40000 fps and resolution of 128×96 pixels.

Theory

Estimation of Temperature Distribution along Film Thickness

Assuming the instantaneous heating of the film by laser irradiation, generation of temperature distribution along the film thickness was roughly estimated introducing the enthalpies of melting and decomposition. In this analysis, effects of the reflection of laser at the film surface, the thermal conduction, the heat radiation, the convective heat transfer and the change in the shape of film during the laser irradiation were neglected. Firstly, distribution of energy density $E(z)$ (J/m^3) provided by the laser irradiation can be described as the function of distance from the film surface z as follows:

$$E(z) = A\alpha \exp(-\alpha z) \quad (6)$$

where A is the fluence of the irradiated laser (J/m^2), and α is the absorption coefficient of the polymer (m^{-1}). The laser fluence can be calculated from the intensity of laser beam I_0 (W/m^2) and its duration Δt (s) as follows.

$$A = I_0 \Delta t \quad (7)$$

Under the assumption of constant heat capacity C_p ($\text{J}/(\text{kg K})$) and density ρ (kg/m^3) of the polymer, local temperature $T(z)$ immediately after the laser

irradiation can be estimated from the energy density as follows.

$$T(z) = T_a + \frac{E(z)}{C_p \rho} \quad T < T_m \quad (8)$$

$$T(z) = T_a + \frac{E(z) - \rho \Delta H_m X_c}{C_p \rho} \quad T_m < T < T_d \quad (9)$$

$$T(z) = T_a + \frac{E(z) - \rho (\Delta H_m X_c - \Delta H_d)}{C_p \rho} \quad T > T_d \quad (10)$$

where T_a is the ambient temperature, T_m and T_d are the melting and decomposition temperatures, ΔH_m is the heat of melting for the polymer of 100% crystallinity, ΔH_d is the heat of decomposition, and X_c is the crystallinity.

Results and discussion

Characterization of the BOPP film

The orientation of PP molecular chain can be conveniently described by birefringence and refractive index. Thickness, three dimensional birefringences and refractive indices, and shrinkage of the as-cast and stretched PP films are summarized in Table 1. By the equi-biaxial stretching to the draw ratio $\lambda_{MD} \times \lambda_{TD}$ of 4×4 , the thickness decreased from 330 to 21 μm . The precursor PP sheets were produced using the film extrusion and casting process setting the take-up speed at a low level to minimize the molecular orientation in the as-cast sheets. Nonetheless, the birefringence between MD and TD (Δn_{MD-TD}) of the as-cast PP sheet showed a small positive value and the refractive index in the MD (n_{MD}) was slightly higher than that in the TD (n_{TD}). These results indicated that there was a slight molecular chain orientation toward MD in the as-cast film.

The equi-biaxially stretched film showed large positive birefringences between MD and ND (Δn_{MD-ND}), and TD and ND (Δn_{TD-ND}). This result indicate the planar orientation of PP molecules along the film surface. On the other hand, the Δn_{MD-TD} showed a small positive value, and the thermal shrinkage in the MD was slightly higher than that in the TD. Therefore, it can be said that the molecular orientation along the film surface was achieved through the equi-biaxial stretching while a slight MD-TD anisotropy of the as-cast film remained in the stretched film.

Laser perforation

When CO_2 laser beam is focused on the BOPP film surface, BOPP film absorbs photon energy from the CO_2 laser. The photon energy is converted to the

Table 1 Thickness, three dimensional birefringences and refractive indices, and shrinkage of the as-cast and stretched PP films.

Draw ratio ($\lambda_{MD} \times \lambda_{TD}$)	Thickness (μm)	Birefringence (Δn) $\times 1000$			Refractive indices (n)			%Shrinkage at 145 °C, 10 s	
		Δn_{MD-TD}	Δn_{MD-ND}	Δn_{TD-ND}	MD	TD	ND	MD	TD
1x1 (As-cast PP)	330	0.6433 ± 0.3235	0.9837 ± 0.6336	0.3404 ± 0.6336	1.4905 ± 0.0003	1.4899 ± 0.0003	1.4896 ± 0.0006	n/a	n/a
4x4	21	0.2708 ± 1.4782	7.3690 ± 2.1554	7.0983 ± 2.1554	1.4925 ± 0.0015	1.4923 ± 0.0009	1.4852 ± 0.0022	28 ± 4	27 ± 0

Fig. 1 A schematic of the laser perforation system with the CO₂ laser source, a mirror and a lens.

thermal energy, and the polymer film can be rapidly heated-up. When sufficient amount of energy is supplied, finally a microhole can be formed through the melting, decomposition and vaporization of the polymer.

Typical SEM images of a microhole formed on a equi-biaxially stretched BOPP film with the $\lambda_{MD} \times \lambda_{TD}$ of 4×4 are shown in Fig. 2. The fluence of applied laser was 142.1 J/cm^2 , which corresponded to the laser pulse duration of $100 \mu\text{s}$. The top-view and cross-sectional view of the microhole shown in Figs. 2-(a) and (b), respectively, indicated that along with the formation of a microhole, a circular rim surrounding the microhole was formed.

Fig. 2 Typical SEM images of a microhole formed on a equi-biaxially stretched BOPP film. The top-view (a) and the cross-sectional view (b) are shown. The fluence of applied laser was 142.1 J/cm^2 , which corresponded to the laser pulse duration of $100 \mu\text{s}$.

Surface morphologies

Effect of the change of laser fluence on the shape of the laser irradiated film surface was investigated using a laser scanning confocal microscope. Series of surface images, and cross-sectional shapes along MD

and TD of the laser irradiated area for the fluences of 49.7 to 142.1 J/cm^2 , which correspond to the laser pulse durations of 35 to $100 \mu\text{s}$, are shown in Fig. 3. For comparison, corresponding SEM images for the cross-section of the laser irradiated area of the film are also inserted.

The trace of laser irradiation could not be detected on the surface of BOPP film up to the fluence of 42.6 J/cm^2 (the laser pulse duration of $30 \mu\text{s}$). The surface deformation of the film was firstly observed at the fluence of 49.7 J/cm^2 ($35 \mu\text{s}$). As can be seen in the figure, a concaved crater surrounded by a circular rim protruding from the film surface was formed. As for the laser perforation, the opening of a circular microhole throughout the film thickness was firstly observed when the fluence was increased to 113.7 J/cm^2 ($80 \mu\text{s}$). Shape of the back-side of the film could not be analysed using a laser scanning confocal microscope, however, observation using a SEM suggested the formation of a “doughnut-like” rim with circular cross-section. Formations of a circular hole and a rim of circular cross-section indicated that the mechanism for the development of such structure is strongly affected by the surface tension.

Variation of the cross-sectional shape in MD of the laser irradiated area with the increase of the fluence of laser pulse is summarized in Fig. 4. Gradual increase of the depth of crater, outward retraction of the rim, and gradual increases of the height and width of the rim as well as the diameter of microhole with the increase of laser fluence were depicted clearly. Analyzing the laser scanning confocal microscope data, variations of the height and width of the rim in MD and TD along with the change of the depth of the crater were obtained and plotted against the laser fluence as shown in Fig. 5. The sizes of the rim as well as the depth of the crater increased with the increase of the fluence, while the size of rim in the MD was slightly larger than that in the TD. This is probably due to the anisotropy of the film with the slightly higher molecular orientation toward MD, which was

Fig. 3 Series of the laser scanning confocal microscope images, and cross-sectional shapes along MD and TD of the laser irradiated area for the fluences of 49.7 to 142.1 J/cm², which correspond to the laser pulse durations of 35 to 100 µs. Corresponding SEM images for the cross-section of the laser irradiated area are also inserted.

Fig. 4 Variation of the cross-sectional shape in MD of the laser irradiated area with the increase of the fluence of laser pulse.

Fig. 5 Variations of the height and width of the rim in MD and TD along with the change of the depth of the crater with the increase of fluence.

depicted in Table 1.

As discussed above, surface tension is considered to be the origin for the formation of a crater/microhole surrounded by a rim, however such difference between MD and TD indicated that the shrinkage originated from the molecular orientation also affect the laser irradiation-induced deformation behavior of film surface.

Effect of laser fluence on microhole diameter and volume loss

As for the laser perforation, the area of microhole was plotted against the laser fluence as shown in Fig. 6. Note that the microhole, i.e. a through-hole along the film thickness, was formed on the BOPP film when the fluence exceeded around 100 J/cm².

Fig. 6 The area of microhole plotted against the laser fluence.

The area of microhole increased rapidly with increasing the fluence to supply additional thermal energy. The maximum microhole diameter reached around 300 μm , i.e. around three times of the diameter of laser beam.

Temperature of the laser irradiated area increases with the increase of the fluence of laser, and eventually thermal degradation and vaporization of the polymer are expected to occur. In order to evaluate such effect quantitatively, the volume loss was also analyzed from the 3D profiles of the laser irradiated area acquired with a laser scanning confocal microscope.

For the volume loss evaluation, a section of the film with the width $\times$ length $\times$ thickness of $400 \times 400 \times 21 \mu\text{m}$ was set as the initial volume. The parts of the deformed area appearing above and below the original film surface correspond to the volume gain and loss, respectively, as shown in Fig. 7. After obtaining each volume through the integration of the data in the designated area, the amount of volume loss was evaluated.

Fig. 7 The parts of the deformed area appearing above and below the original film surface. The upper and lower parts correspond to the volume gain and loss, respectively.

As described previously, the laser scanning confocal microscope could evaluate the shape of the top surface of the film only, while the rim showed a “doughnut-like” shape with circular cross-section as shown in Fig. 2. Even before the opening of a microhole, there can be a starting of the deformation on the back-side of the film. Considering these factors, the assumption that the bottom surface of the film exhibits the same shape as the top surface was made for the analysis of volume loss. This assumption corresponds to the relatively low absorption coefficient of the film. For the sake of the consistency of data analysis, the same assumption was applied even when the depth of the crater was larger than

Fig. 8 Variation of volume loss with the laser fluence.

the half of the film thickness. In this case, there can be an overestimation of the volume loss.

The results of volume loss analysis for various laser fluences are shown in Fig. 8. It is obvious that the volume loss was close to zero up to the fluence of around 150 J/cm^2 . In this region, even though the formations of a crater and a rim were clearly observed, the volume elements of material above and below the film surface were similar. With the further increase of the fluence, the volume loss showed a significant increase and reached to 14.30% at the laser fluence of 426.3 J/cm^2 . The volume loss of 14.30 % corresponds to the actual amount of volume loss of ca. $480,000 \mu\text{m}^3$, which is equivalent to the cylindrical volume element through-out the film thickness with the diameter of ca. 170 μm .

It should be noted that there was a tendency of saturation for the increases of microhole diameter and volume loss with the increase of laser pulse fluence when the fluence exceeded around 150 J/cm^2 as can be seen in Figs. 7 and 8.

Estimation of film temperature during laser processing

As described in the THEORY section, in the analysis of temperature distribution immediately after the cessation of laser irradiation, effects of the reflection of laser at the film surface, the thermal conduction in the film, the heat radiation and the convective heat transfer from the film surface, and the change in the shape of film during the laser irradiation were neglected.

The validity of these assumptions can be broadly discussed as follows. It is known that the emissivity of thick polymeric materials is around 0.9 or higher, which corresponds to the reflectivity of around 0.1 or less. In addition, the thermal diffusion distance for 1 s of ordinary polymer is known to be around 1 mm. Because time for the thermal diffusion is proportional to the square of distance, during the pulse duration of

100 μs , the thermal diffusion distance is estimated to be only around 10 μm . Furthermore, effect of the heat radiation can be roughly estimated based on the Stefan-Boltzmann law. Even at the temperature of 600 $^{\circ}\text{C}$ and the emissivity of 1.0, estimated heat radiation $P = \sigma A T^4$, where σ is the Stefan-Boltzman constant ($\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$), for the circular area of diameter 100 μm is only $3 \times 10^{-4} \text{ W}$. At the temperature of 600 $^{\circ}\text{C}$, normally effect of convective heat transfer is much smaller than the effect of heat radiation. Therefore, effects of the surface reflection of laser, the thermal conduction, the heat radiation, and the convective heat transfer during the duration of laser irradiation are considered to be almost negligible.

Thermal decomposition behavior of the BOPP film analysed using the TGA is shown in Fig. 9. Because the thermal decomposition is a kinetic process, the apparent starting point of thermal decomposition shifted to higher temperatures with the increase of heating rate. For the sake of simplicity, we defined the thermal decomposition temperature as the temperature where the weight reduction reached 5%. From the data shown in Fig. 9, thermal decomposition temperatures for the heating rates of 10, 100 and 200 K/min (0.167, 1.67 and 3.33 K/s) were estimated to be 395, 436 and 445 $^{\circ}\text{C}$. Using these data, the thermal decomposition temperature during the laser irradiation was roughly estimated through the extrapolation of the logarithm of heating rate versus thermal decomposition temperature relation. The calculated heating rate of the film with the continuous irradiation of laser was 4.5 K/ μs , and the thermal decomposition temperature at this heating rate was estimated to be 686 $^{\circ}\text{C}$.

Fig. 9 Thermal decomposition behavior of the BOPP film analysed using a TGA.

Variation of temperature distribution along the film thickness with the increase of laser pulse fluence was estimated based on the equations (8)–(10). For the

calculation, the heat capacity C_p of 2.1 J/gK, the density ρ of 0.9 g/ cm^3 , the heat of melting ΔH_m of 209 J/g, and the absorption coefficient α of 6.2 /cm were adopted from the literature [21]. The crystallinity X_c of 45.3 % and the heat of decomposition ΔH_d of 856 J/g were obtained from the DSC and the TGA measurements, respectively.

The estimated temperature distributions along film thickness for various laser fluences are shown in Fig. 10. Because of a relatively low value of absorption coefficient, temperature difference between the top and bottom surfaces of the film of 21 μm thick was only about a few degrees.

Fig. 10 Estimated temperature distributions along film thickness for various laser fluences.

It was found that the temperature of the film surface reaches the melting temperature ($T_m = 164.7^{\circ}\text{C}$) at the laser fluence of 42.6 J/ cm^2 . With the increase of fluence, the increase of temperature stops for a while because the supplied energy is consumed for the melting of the polymer. After the complete melting, the temperature starts to increase again, and reaches the thermal decomposition temperature ($T_d = 686^{\circ}\text{C}$) at the laser fluence of 198.9 J/ cm^2 . The behavior of temperature increase similar to the one at the melting temperature should occur when the temperature reaches the thermal decomposition temperature.

Comparison of the theoretically estimated temperature with experimental results

Starting of the deformation of film surface observed at the laser fluence between 42.6 and 49.7 J/ cm^2 matched well with the theoretically

estimated fluence for the surface to reach the melting temperature of 42.62 J/cm^2 . At the fluence of 49.7 J/cm^2 the estimated film temperatures at the top and bottom surfaces were 168 and $166 \text{ }^\circ\text{C}$, respectively.

On the other hand, the experimentally obtained laser fluence of 113.2 J/cm^2 for the formation of a microhole corresponds to the estimated temperatures of the top and bottom surfaces of 377 and $373 \text{ }^\circ\text{C}$, respectively. It should be noted that these temperatures are below the temperature for the starting of thermal decomposition even for the heating rate of 10 K/min . In other words, it can be said that the microhole was created without the effect of thermal decomposition.

The theoretically estimated surface temperature reached the decomposition temperature at the laser fluence of 198.9 J/cm^2 , while the experimental results indicated that the steep increase of volume loss started when the laser fluence exceeded around 150 J/cm^2 . The discrepancy between the theoretical estimation and experimental results in terms of the temperature for the starting of thermal decomposition suggested the overestimation of the thermal decomposition temperature. It should be noted that the film temperature can stay at the elevated level after the cessation of laser irradiation, which may induce further decomposition of the polymer irrespective of the heating rate.

As described previously, there was a tendency of saturation for the increases of microhole diameter and volume loss with the increase of laser pulse fluence. These facts may suggest that the opening of the microhole proceeded quickly during the duration of laser pulse irradiation.

In-situ observation of Microhole formation

To investigate the relation between the duration of laser irradiation and the timing of microhole opening, in-situ observation of the deformation behavior of the film during the laser perforation process was carried out using a high-speed video. The speed for the image capturing of 40000 fps corresponds to the interval between the images of $25 \mu\text{s}$. Typical example of the series of images depicted for the laser pulse fluence of 142.1 J/cm^2 , i.e. laser pulse duration of $100 \mu\text{s}$, is shown in Fig. 11. From the captured video images, the time-dependent hole radius was evaluated as shown in Fig. 12.

It should be noted here that because the carbon dioxide laser is not visible in the video images, the

Fig. 11 Typical example of the series of high-speed video images depicted for the laser pulse fluence of 142.1 J/cm^2 . The time for the starting of deformation was arbitrarily set to $25 \mu\text{s}$.

Fig. 12 Variation of microhole radius with time for the laser fluence of 142.1 J/cm^2 .

moments of starting and ending of laser irradiation could not be judged. Therefore, the elapsed time for the image with the first appearance of the effect of laser irradiation was arbitrarily set to $25 \mu\text{s}$.

The results revealed that the time difference between the appearance of surface deformation ($25 \mu\text{s}$) and the opening of a microhole ($75 \mu\text{s}$) is $50 \mu\text{s}$. This time difference agreed well with the result shown in Fig. 4, i.e. the difference in the duration of laser for the starting of deformation ($35 \mu\text{s}$) and the opening of a microhole ($80 \mu\text{s}$) of $45 \mu\text{s}$. On the other hand, the speed of microhole opening at the initial stage of 25 to $50 \mu\text{s}$ was found to be extremely fast followed by rather slow expansion as shown in Fig.12.

The speed of the expansion at the initial stage was estimated to be around 0.6 m/s. These facts suggested that the opening of a microhole started to occur without much delay after the temperature reached the melting temperature, even during the duration of laser irradiation. If a microhole opens at the center of laser beam, the laser beam can not be absorbed by the film, and eventually efficiency of laser irradiation decreases. This can be one of the reasons for the tendency of saturation in the increases of microhole diameter and volume loss with the increase of laser fluence shown in Figs. 7 and 8.

During the laser irradiation, significant radial temperature distribution arises with the highest temperature at the center of the laser beam. When the temperature of the polymer reaches above the melting temperature, distributions of viscosity and surface tension are also generated with the lowest viscosity and the lowest surface tension at the center. These are considered to be the origin of the microhole opening and formation of the rim surrounding the microhole.

Generation of temperature distribution also induces thermal conduction from the center part of laser irradiation to the peripheral region. It should continue after the cessation of laser irradiation, which may cause further expansion of the size of microhole as well as the enlargement of the surrounding rim. Along with the thermal conduction, heat transfer from the film surface to the ambient also should occur, and eventually film temperature cools down, and the microhole expansion stops.

Conclusions

Equi-biaxially oriented polypropylene films were perforated by the CO₂ laser under various laser fluences. With the increase of fluence, the surface deformation with the formation of a crater surrounded by a doughnut-like rim was firstly observed followed by the formation of a microhole surrounded by the rim. The sizes of the microhole and rim increased rapidly with the increase of laser fluence. Mechanism for the formation of a crater/microhole surrounded by a rim was discussed based on the effects of the surface tension and the shrinkage. The starting of the rapid increase of volume loss was delayed in comparison with the opening of a microhole. The velocity of microhole opening increased rapidly presumably during the

laser irradiation, and then slowed down after the cessation of laser irradiation. Comparison of the theoretically estimated temperature of the film and the laser perforation behavior revealed that the starting of the deformation of film matched well with the starting of melting of the film surface, the film temperature was lower than the thermal decomposition temperature at the moment of the opening of a microhole, and the film temperature was lower than the decomposition temperature at the moment of the starting of volume loss.

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