Ablation of Polypropylene for Breathable Packaging Films

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Abstract

A Polypropylene (PP) film was ablated using a femtosecond laser with a center wavelength of 785 nm, a pulse width of 184 fs and a repetition rate of 1 kHz. Increments of both pulse energy and the shot number of pulses lead to co-occurrence of photochemical and thermal effect, demonstrated by the spatial expansion of rim on the surface of PP. The shapes of the laser-ablated PP films were imaged by a scanning electron microscope (SEM) and measured a 3D optical measurement system (NanoFocus). And, the oxygen transmission rate (ORT) of periodically laser-ablated PP film were characterized by oxygen permeability tester for modified atmosphere packaging (MAP) of fresh fruit and vegetable. Our results demonstrate that femtosecond pulsed laser is efficient tools for breathable packaging films in modifying the flow of air and gas into and out of a fresh produce container, where the micropatterns are specifically tailored in size, location and number which are easily controlled by laser pulse energy and pulse patterning system.

Key words : Femtosecond laser ablation, Polypropylene, Modified atmosphere packaging

1. Introductions

Laser ablation with femtosecond lasers is sufficiently promising for microfabrication of materials. For instance, a thermal affected zone was not formed in the ablated area even for metals [1]. Also, the high peak power of fs lasers could induce a multiphoton absorption to ablate transparent materials [2]. Similar results were also obtained in the case of polymer [3-6]. With the advance of femtosecond laser technology and polymer science, femtosecond laser-polymer interaction has been attracting more and more attention, and has recently directed polymer applications to fabricating microelectronic components and optical devices, according to their specific thermal, electrical, mechanical and chemical properties [7]. It has also been demonstrated that transparent polymers can be processed with ultrashort laser pulses. This indicates that nonlinear absorption and/or incubation effects play an important role. The detail ablation mechanism is still under discussion. It is also well known that femtosecond laser processing has great potential for ablation on polymers, two-photon polymerization, and direct writing [8-12].

Polypropylene (PP) has been widely used in the packaging industry because of its highly adaptable properties and good thermal stability, chemical resistance, physiological compatibility. And, the micro-perforated PP film relates to the field of packaging for respiring or biochemically active agricultural products such as fresh fruits, fresh vegetables, fresh herbs, and flowers and more particularly for use in modifying the flow of oxygen and carbon dioxide into and/out of a fresh produce container. In this paper we present ablation results of PP films using a 785 nm femtosecond laser, and experimentally observe the ablation depth and width at different pulse energy and number. Finally, it is first time, for our knowledge, we have demonstrated femtosecond laser micro-patterned packaging films for modifying atmosphere packaging (MAP).

2. Experiment and results

The femtosecond laser processing system with a pulse duration of 184 fs, a repetition rate of 1 kHz and a pulse energy of 1 mJ at λ=785 nm was used for the ablation experiment in air. The laser pulses were guided into a microscope and focused by a plano-convex lens with focal length of 100 mm. The average power of the laser beam is controlled by motorized attenuator inserted between the laser and the focusing lens. The sample is translated by a computer-controlled three-dimensional stage at a resolution of 100 nm. The features produced during focused irradiation of femtosecond pulses are observed through a CCD camera mounted upon the microscope.

It was reported that when a pulsed UV laser irradiates on the surface of an organic polymer, depending upon the incident wavelength, pulse number and pulse energy, a range from several hundred nanometers to tens micron on the surface of the material could be ablated away with a geometry that is defined by the incident laser beam.

Oriented polypropylene(OPP) films with a thickness of 30 um, which run well over a wide range of temperatures and have good clarity and printability, were prepared for ablation. Figure 1 shows the microscope SEM image of OPP film ablated by a femtosecond laser with the pulse energy of 1.9 uJ, 27 uJ and 108 uJ. As can be seen in Fig. 1, OPP film was successfully ablated with a femtosecond laser pulse. At 160 uJ, the ablation width was approximately 31 um. Threshold is the minimum pulse energy per unit area needed to initiate the ablation process and is specific for every material. The threshold of OPP film was measured by patterning the surface with various pulse energies with a single pulse. An optical microscope was used to determine ablation threshold, defined as the pulse energy corresponding to an observable damage of the target surface. The threshold fluence was determined to be 2.9 J/cm^2 with 785 nm and 185 fs laser pulses at the beam diameter of 5.6 mm and the focal length of 100 mm. The ablation depth of 20 um was measured by a optical measurement system (NanoFocus). In Fig. 2, the ablation width and depth versus pulse energy are shown for OPP film. For the OPP film ablated, the ablation width of the crater was increased with higher pulse energies but the depth was limited to near 23 um above the pulse energy of 300 uJ. The image of the laser-patterned polypropylene films were characterized using a optical microscope and optical measurement system (NanoFocus).

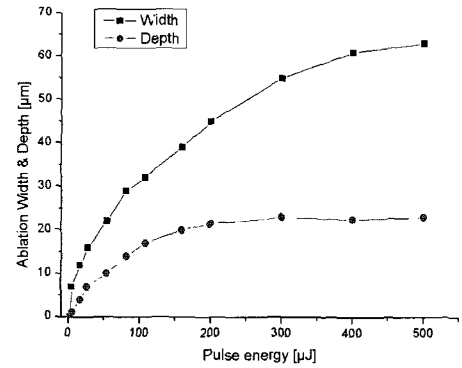
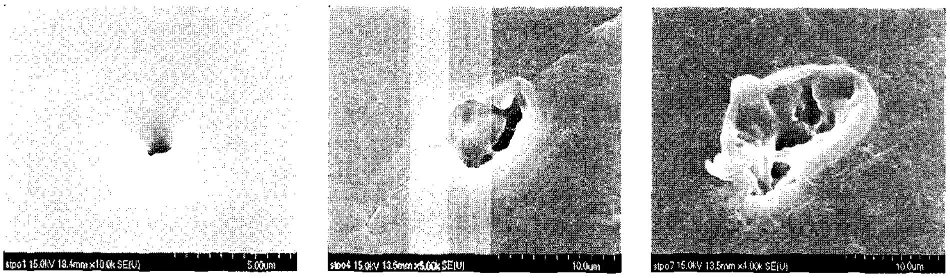


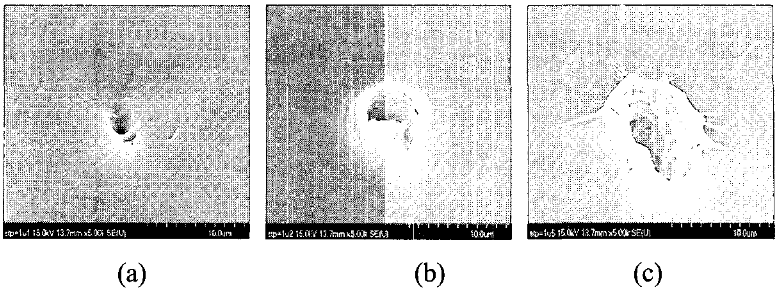
Fig. 2 Ablation width and depth versus pulse energy with one femtosecond laser pulse.

For further investigation the pulse number N was varied using a synchronized pulse switching system (Lasermetrics 5100EW 50kHz). Figure 3 show the SEM image of the OPP film surface ablated with wavelength of the 785 nm and pulse energy of 5.5 uJ. When the pulse number



(a) (b) (c)

Fig. 1 SEM image of OPP film ablated by a femtosecond laser with the pulse energy of (a) 1.9 uJ, (b) 27 uJ and (c) 108 uJ.



(a) (b) (c)

Fig. 3 SEM image of OPP film ablated by a femtosecond laser with the pulse energy of 5.5 uJ. (a) 1 pulse, (b) 2 pulses and (c) 5 pulses.

was 1, 2, and 5, the ablation width/depth were 5.5/1.5, 9.7/4.5, 11.6/13.9, respectively. After the first pulse was deposited, the ablation depth was determined to follow a linear relationship with the successive pulses. We measured the ablation width and depth per pulse number with a fs laser at the same pulse energy and various pulse number. The image of the laser-patterned polypropylene films were observed by a scanning electron microscope (SEM). With an increasing number of applied laser pulses (N>5), the rim around the ablated craters is observed on OPP, as can be seen in Fig. 3(c), which shows the SEM image of a crater of OPP irradiated by single and multi-shot laser with a pulse energy of 5.5 uJ. When the polypropylene is irradiated by a femtosecond laser with a pulse energy higher than ablation threshold, occurrence of ablation is mainly caused by the direct dissociation of molecules from the excited electronic states induced by absorbing laser photons. Meanwhile, the irradiation process co-presents a relaxation process that eventually converts photon energy into thermal energy. Therefore, different decomposition pathways will occur due to both photochemical and thermal effects. As can be seen in Fig. 3, formation of the rim is attributed to polymer melting and thereafter spreading across the crater. The driving force may result from surface tension due to a temperature gradient and a back pressure over the crater. It is therefore deducible that the spatial expansion of the rim is caused by growing mobility of the melt as a result of increasingly accumulated heat as the pulse energy and the number of pulses increase.

Figure 4 shows the ablation width and depth of the crater versus the pulse number for linear polarized pulses with duration of 184 fs. The pulse number was

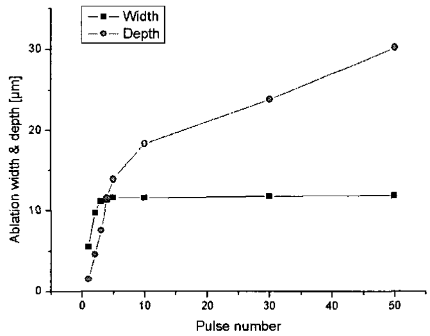


Fig. 4 Ablation width and depth versus pulse number with a femtosecond laser pulse energy of 5.5 uJ.

increased from N=1 to N=50 at a fixed pulse energy of 5.5 uJ. The ablation width changes significantly during the first 5 laser pulses. For N>30 the ablation widths are nearly constant. And, the ablation depth of the crater was increased with higher pulse numbers. Average ablation depths per pulse of 0.6 um were obtained at the same pulse energy (slope of the approximately linear fit in Fig. 4). The image of the laser-patterned polypropylene films were characterized using a scanning electron microscope (SEM) and optical measurement system (NanoFocus).

The quality and shelf life of many food products is enhanced by enclosing them in packaging that modifies the atmosphere surrounding the product. Modified atmosphere packaging (MAP) is a method for controlling the flow of air and gas into and out of a fresh produce container. For MAP of fresh fruits and vegetables is to microperforate polymeric packaging materials. Various methods can be used to microperforate packaging materials: cold or hot needle mechanical punches, electric spark. Mechanical punches are slow and often produce numerous large perforations (1 mm or larger) throughout the surface area of the packaging material. Also, equipment for spark perforation of packaging materials is not practical for most plastic converting operations. The most efficient and practical method for making microperforated packaging materials is using laser. For this applications, thin OPP films were micro-patterned using a femtosecond laser pulsed laser. Polypropylene (PP) film is the most commonly used packaging in food and vegetable packaging. The oxygen transmission rate (OTR) of fs laser microperforated films were measured by a oxygen permeability tester (PBI Dansensor, OPT-5000). The OTR is expressed as cc $O_2/m^2 \cdot day \cdot$ atmosphere, where the reference of OPP films with 30 um thickness is 1503 cc /m2·day·atm. This OTR, however, is much too low to preserve the fresh quality of high respiring produce items like fruit and vegetable. Therefore, several approaches have been researched describing methods to produce packaging materials to accommodate the higher respiration rate requirements of a wide variety of fresh produce items. Generally, OPP films with OTRs of 5,000 to 50,000 $cc/m^2 \cdot day \cdot$ atm are needed for fresh fruit and vegetable packaging. Figure 5 shows the OTR of fs laser micropatterned film with having 100 to 25 micropatterns per cm^2 with mean diameters of 24 um to 63 um and depth of 17 um to 23 um. OPP films with a thickness of 30 um were prepared for ablation. The beam has a wavelength of 785 nm, pulse duration of 184 fs and repetition rate of 1 kHz. The laser beam

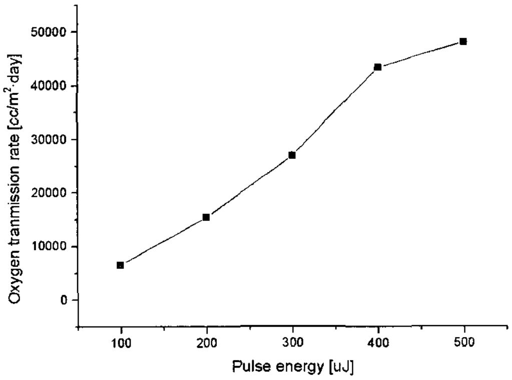


Fig. 5 Oxygen transmission rate of micro-patterned OPP film with 100 micro-patterns per square centimetr.

was focused by a objective lens with a focal length of 100 mm. Micropatterns were created by fs laser pulses train, where each pulse are create each patterns with processing speed of 1 kHz bit/s. This fs laser pulse pattering method is very efficient for math product of micropatternd film. Further, the ablation width and depth of micropatterns are adjusted by using the pulse energy, and number of micropatterns are optimally selected to obtain the desired gas transmission rate for maintaining the quality of that specific produce item. As a result, our results demonstrate that femtosecond pulsed laser is excellent tools for microperforated packaging films in modifying the flow of air and gas into and out of a fresh produce container, where the micro-patterns are specifically tailored in size, location and number required.

3. Conclusions

We present ablation results of polypropylene films using a 785 nm femtosecond laser, and experimentally observe the ablation width and depth at various pulse energy and number. As pulse energy and the number of pulses increase, thermal effect and photochemical reaction coexist as mechanisms operative during polypropylene ablation process using a femtosecond laser. For modified atmosphere packaging, thin oriented polypropylene films were micropatterned using femtosecond laser pulses. As a result, we have demonstrated femtosecond laser microperforated packaging films for extending the quality and shelf life of respiring foods, particularly fresh fruits and vegetables contained within packaging.

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