

Laser Etching of Polymer Compounds

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ABSTRACT: Laser etching of carbon black-loaded polypropylene compounds was studied by using a Nd : YAG laser of 532 nm wavelength. A mathematical equation was developed to describe the etching process. The etching experiments showed that, under certain laser conditions, the width and depth are only affected by the carbon black. There was quantitative agreement between the theoretical prediction and the experimental results. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2119–2123, 1998

Key words: laser etching; carbon black; polypropylene; fluence threshold

INTRODUCTION

Photo ablation of polymers was first investigated in 1982 by Srinivasan.¹ Much work has been focused on the photoablation of polymethylmethacrylate (PMMA) and polyethylene terephthalate (PET), which have special characteristics under the action of lasers. In these polymers, a photochemical process dominates the photo ablation when a pulsed laser of short wavelengths (~ 200 nm) is used, and the thermal process becomes important at long wavelengths (~ 500 nm). Kim and Postlewaite investigated the ablation of PMMA under a 532-nm laser.² They concluded that the ablation process was accompanied by abrupt heating, whereas the photochemical process had little effect, and ablation is thus the result of thermal decomposition.

Reaction of polymer compounds under pulsed laser with a long wavelength is just beginning to attract attention. In fact, some polymers (for example, polypropylene (PP) and PE) are transparent to a quite wide range of wavelengths.

When small amounts of photosensitive fillers are added to these polymers to form polymer compounds, black-white and color-marking effects can be generated under a laser.^{3,4}

We present in this article a mathematical model for carbon black (CB)-loaded PP under long wavelength laser radiation in order to describe the etching process. Comparison of experimental results with the theoretical values gave quantitative agreement.

THEORETICAL MODEL

For most polymers, photo-absorption of laser follows Beer-Lambert's law. However, it has been rarely studied whether or not the law holds also for CB-filled polyolefin. For these compounds, we assume first that (1) for the base materials, there is only one absorption coefficient; (2) the surface reflection is neglected; (3) the filler particles (for example, CB) are spherical and uniformly dispersed in the sample; and (4) the photons are absorbed by CB particles when they collide with the CB particles.

From Beer-Lambert's law, the relationship between etching depth l and fluence F_l is described as

$$F_{th} = F_l \exp(-\alpha l) \quad (1)$$

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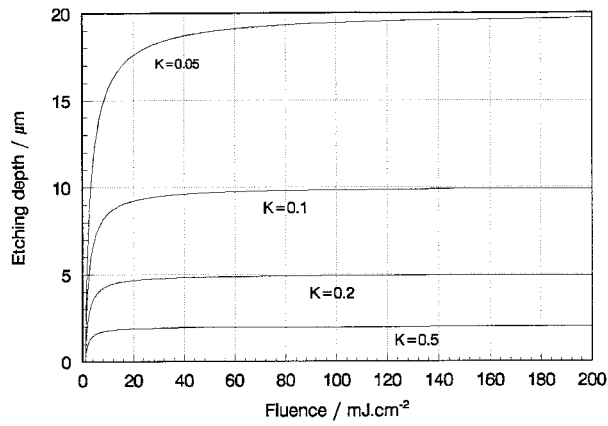


Figure 1 Theoretical curve of the etching depth versus the fluence for different K for PP-CB compounds:

$$F_l = F_{th} \frac{\exp(\alpha.l)}{1 - Kl}, F_{th} = 1 \text{ mJ.cm}^{-2}, \alpha = 0.05 \text{ } \mu\text{m}^{-1}.$$

where F_{th} is a threshold values for the fluence, at which the hole formation just starts or stops, respectively. F_{th} is also defined more precisely hereafter as the fluence value at which the etching width is equal to the laser beam diameter R . α is the absorption coefficient of the compound, which describes the attenuation rate of the light.

Suppose the probability of photons absorbed by CB particles is P ,

$$P = \rho V = \pi(r + R)^2 l \rho = Kl$$

$$K = \pi(r + R)^2 \rho \quad (2)$$

Here, ρ stands for the particle number per unit volume. Hence, the empirical eq. (1) of the light attenuation in the sample is changed to

$$F_{th} = F_l(1 - Kl)\exp(-\alpha.l) \quad (3)$$

or

$$F_l = F_{th} \frac{\exp(\alpha.l)}{1 - Kl} \quad (4)$$

In this equation, K is related to the number (for example, density), the size, and the distribution of the fillers. F_l is the initial value of input laser fluence, which leads the final etching depth to be l .

Figure 1 shows the theoretical curve of etching depth l versus F_l drawn according to eq. (4) with respect to K . All the l curves tend to their own limits, respectively, demonstrating that when a

pulse of laser radiation with fluence above a threshold value, for instance of 1 mJ cm^{-2} , falls on the polymer compound, the material at the irradiation site, for example, on the surface, is spontaneously etched away to a depth of some micrometers. The etching depth depends strongly on the parameter K . K takes into account the effects of ρ , r , and R . In general, r and R are constants; thus, a large K value is in agreement with large ρ , showing the sample is densely filled with CB particles. Adjacent CB particles make the light difficult to disperse into further regions. Therefore, it can be easily understood why the value of l decreases with increasing K .

The same l - F_l tendency also appears in Figure 2 for parameter α . Under the same loading level, the depth will decrease with the increase of absorption coefficient. Experimental spectral analysis gave a low value of absorption coefficient of pure PP; thus, the most light can transmit through the PP film and comes into collision with CB. Heat is spontaneously produced, leading to a surface ablation. The extreme rapidity of the process excludes the transfer of light and heat beyond the dimension of the first ablated thin layer.

EXPERIMENTAL

A Nd : YAG laser was used in this work emitting a pulse of 12-ns half-width at a wavelength of

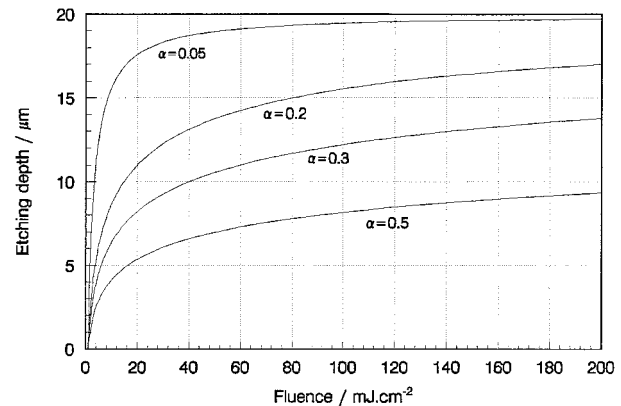


Figure 2 Theoretical curve of the etching depth versus the fluence for different α for PP-CB compounds:

$$F_l = F_{th} \frac{\exp(\alpha.l)}{1 - Kl}, F_{th} = 1 \text{ mJ.cm}^{-2}, K = 0.05 \text{ } \mu\text{m}^{-1}.$$

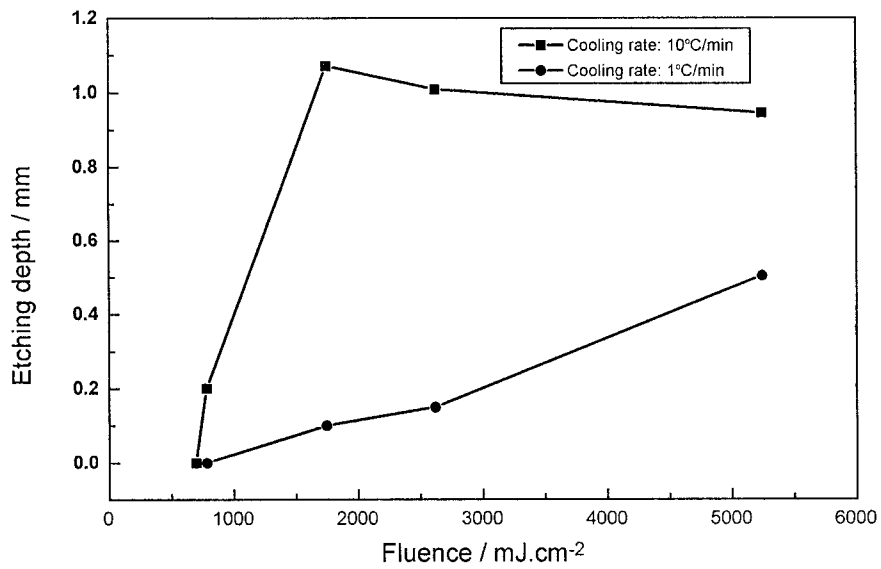


Figure 3 The etching depth versus the fluence of PP for different cooling rates.

532 nm. The laser beam was focused by a 45-mm aperture. The diameter of the beam was 0.27 mm. The pulses had Gaussian characteristics. The en-

ergy was monitored by a LPE-1A numerical energy gauge.

Polypropylene (MFI = 11.6 g/10 min, 230°C/

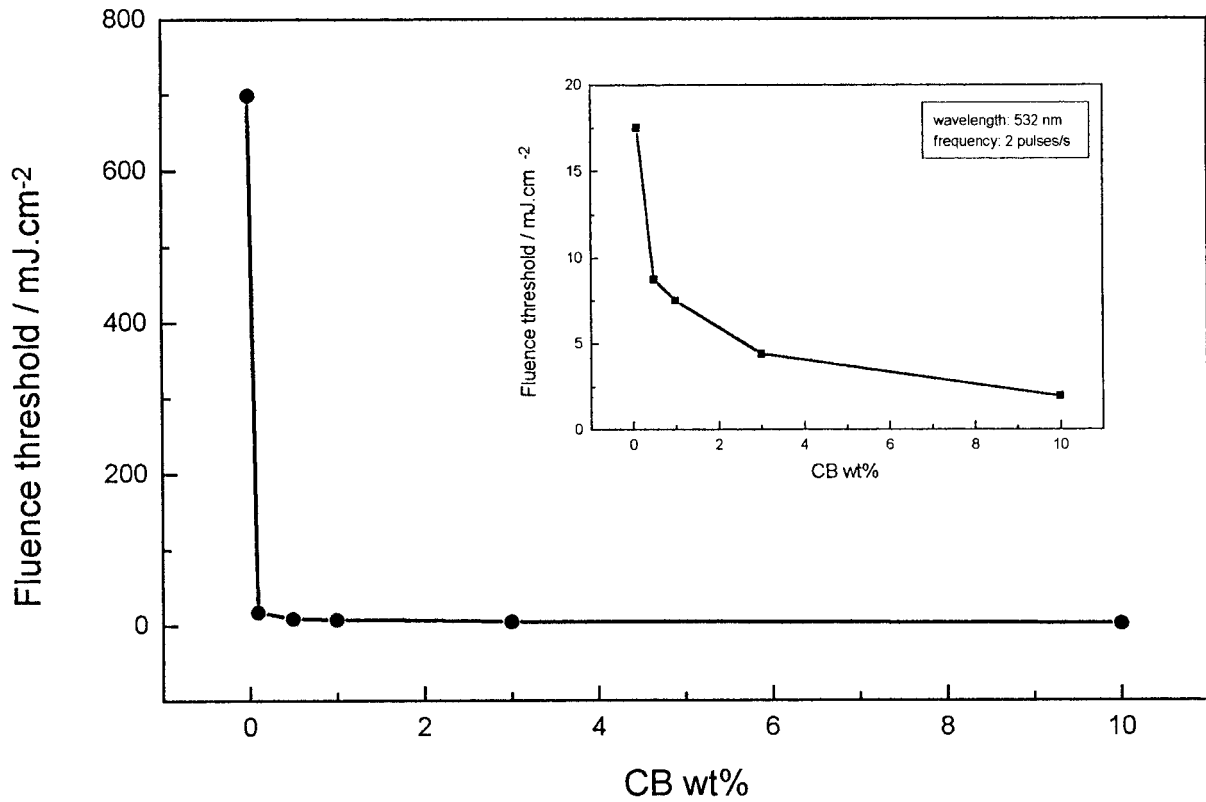


Figure 4 The fluence threshold versus the CB weight fraction for PP-CB compounds.

2.16 kg; Yanshan Petrochemical Co., China). Both pure PP and the PP–CB samples, which were previously shear-milled on a double-roller machine, were hot-pressed to plate samples of 3 mm thickness at 170°C for 10 min. The samples were exposed to such pulses, respectively, and scanned by the laser at 0.33 mm/s. The etching depth and width were measured by a XJZ-6 microscope produced by Jiangnan Optical Instrument Plant, China.

RESULTS AND DISCUSSION

Figure 3 shows how the etching depth of the pure PP increases with the fluence for two cooling rates, which influence the crystallinity and grain size of the polymer. The depth rises steadily, almost linearly, for the sample prepared at a lower cooling rate of 1°C/min; whereas for that cooled at 10°C/min, it increases rapidly in the first range of the fluence, reaching a maximum at 1800 mJ cm⁻², then it falls slightly.

It is obvious that both curves for the semicrystalline PP cannot be fitted by Beer–Lambert's law, in contrast to many other polymers, such as PMMA, PC, PET, and PI, where this law is obeyed.⁵ Experimentally, it was very difficult to etch polymers with higher crystallinity.

By adding 0.10 wt % CB as a laser absorbent into the PP, the fluence threshold decreased dra-

matically from 699.00 to 17.48 mJ cm⁻² due to the strong light absorption of the CB particles (Fig. 4). The higher the weight fraction of the CB added, the lower the threshold. The dominating function of CB particles in PP in the case of the laser etching made it indifferent to the crystallinity of the base polymer, caused by different cooling conditions.

Figure 5 shows the change of the etching width and depth of the compounds versus the fluence for two loading levels, respectively. Both width curves increase with the fluence: the more the CB filler, the wider the etched pit. The level line indicates the beam diameter of the laser. The etching depth being smaller than the diameter is predicted by the theoretical model, the both curves tend to their own limits, respectively, for the two loading levels.

However, the depth curves differ significantly from each other. The theoretical model predicts a decrease of the depth with increased CB loading, as well as the absorption coefficient. But in the experiment, when the sample was highly filled with 10 wt % CB, etching depth leveled out with the fluence and remained constant thereafter, with a steady dip at 35 mJ · cm⁻²; then it fell even into the negative range. The l – F_l curve for the sample with low filler content (0.1 wt %) appears to follow the theoretical curve approximately. The maximum depth limit was against 28 μm up to 42 mJ · cm⁻².

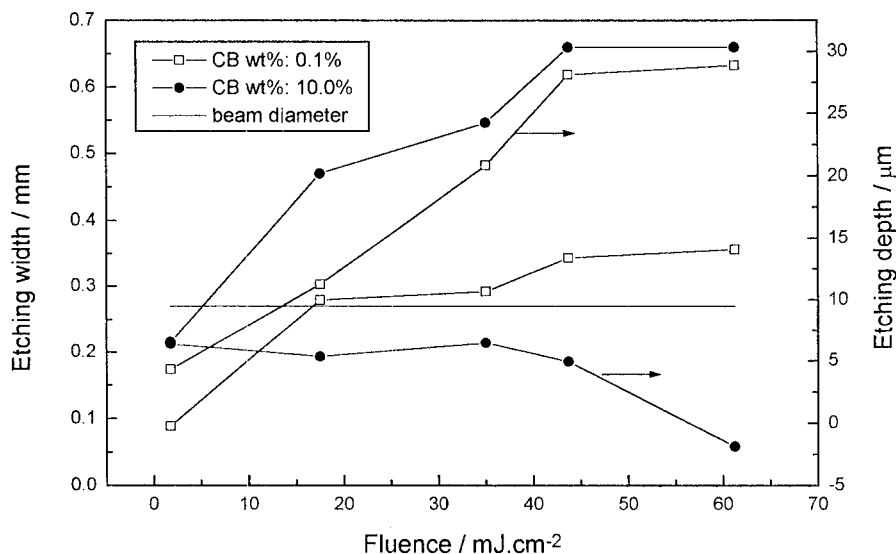


Figure 5 The etching width and depth versus the fluence for PP–CB compounds.

Why does the pulsed 532 nm wavelength radiation cause a thin and wide etch region for the highly filled sample, while results for the low filler content give a deep and narrow region? One reasonable possibility is thermal ablation. During such a short pulse, the temperature ΔT produced is as high as

$$\Delta T = \frac{F_l \cdot \pi \cdot r^2}{\frac{4}{3} \pi \cdot r^3 \cdot \rho \cdot C_p} \approx 5000^\circ\text{C}$$

where $F_l = 1 \text{ mJ/cm}^2$, $r = 1 \text{ mm}$, $\rho_{\text{CB}} = 2 \text{ g/cm}^3$, $C_p = 2.038 \text{ cal/(mol} \cdot ^\circ\text{C)}$. The high temperature decomposes the polymer around the CB particles, leading to an explosive volume expansion of the irradiating areas. Since the lifetime of the excited CB is so short, the first layer quickly thermolyses the absorbed light energy, and is immediately ablated.

The process depends on the location of CB particles. For low filler content compound, photons may collide with the particles over a greater depth; whereas for highly filled one, the opposite is true. This behavior has qualitatively been predicted by eq. (2) shown in Figures 1 and 2. Moreover, when the sample was densely filled (e.g., with 10 wt % CB), the exposed surface was found to be foamed. An interaction among heat flow, volume expansion, and back pressure may be responsible for the foam. The ablation process can be visualized as being similar to exhausting gases from a rocket. The decomposed, explosively expanded fragments and CB particles rush out, producing a back pressure nearly normal to the ablation pit. The further expansion is thus suppressed.

CONCLUSION

A mathematical model was formed to predict the etching behavior of polymer compounds under a

pulsed laser with a long wavelength. The main factors affecting the process were analyzed. Etching depth increases exponentially with the laser fluence, depending significantly on parameter K and α , related to the size, density, distribution, and the absorption ability of the laser absorbent filler in the polymers. The deviation between the theoretical and experimental results is attributed to the boundary conditions.

When PP-CB compounds were exposed under the laser, photons were immediately absorbed by CB particles, leading to surface ablation. The process was dependent on the manner in which the CB dispersed in the base polymer. Interaction of high temperatures in a short pulse produced polymer decomposition, explosive expansion, and high back pressure, which dictated the etching results. Quantitative agreement between the theoretical prediction and experimental results was shown.

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