Surface Microstructure Formation by ps- and fs-Laser Ablation of an Elastomer Composite

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SUMMARY: We investigated the laser ablation of an elastomer composite with picosecond- (ps-) and femtosecond- (fs-) pulsed UV lasers (ps-laser: $\lambda = 263$ nm, $\tau = 8$ ps; fs-laser: $\lambda = 248$ nm, $\tau = 500$ fs). Upon laser irradiation, a unique microstructure on the surface of the elastomer composite (acrylate polymer) containing carbon black (particle size: 18-30 nm) was observed. The laser-ablated surfaces were analyzed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The formation mechanism is discussed in terms of thermal effects induced by the different pulse durations of the lasers.

Introduction

Laser ablation has been used to produce morphological microstructures on the surface of polymer films [1, 2)], which help to improve adhesive bonding, control surface friction, and align liquid crystals [3)]. Recently, we observed the formation of a microstructure containing carbon black on the surface of an elastomer composite (acrylate polymer), upon the irradiation with a nanosecond- (ns-) pulsed UV laser at a wavelength (λ) of 248 nm with a pulse duration (τ; full-width half maximum (FWHM)) of 30 ns. A micron-ordered tip-like structure appeared on these laser-ablated surfaces after laser ablation, and with increases in the number of laser pulses the size of the microstructures became larger by 20–30 μm on the irradiated surfaces. We proposed a mechanism for this microstructure formation based on the aggregation of carbon-rich debris on the top of the microstructures during ablation [4)]. In the present study, we investigated the laser ablation of the elastomer composite using picosecond- (ps-) and femtosecond- (fs-) pulsed UV lasers in order to examine further this formation mechanism. The aggregation of carbon particles is likely to be highly influenced by the duration of the

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laser pulse. Moreover, at wavelengths of ca. 250 nm, the carbon particles should be highly absorbent for the photon, whereas absorption by the acrylate polymer should be negligible based on single-photo absorption. Thermal energy diffusion to polymer matrix from carbon particles is also expected to play a key role in the ablation.

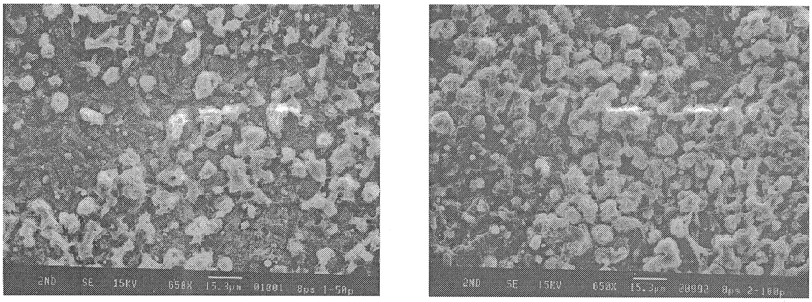
Experimental

Sheet samples of elastomer containing carbon black were prepared by mixing 100 parts of acrylate polymer ($-(CH_2\text{-}CH\text{-}(CO\text{-}O\text{-}R)\text{-})_n\text{-}$, R=$C_4H_9$, $C_2H_4OCH_3$)(Nippon Mektron, PA404K) and 50 parts of carbon black (ISAF grade, particle size: 18-30 nm). This mixture was kneaded with rollers and vulcanized after a vulcanizing agent and accelerator were added, and was finally compressed into sheet form under 100 kgf·cm^{-2} through pre-curing at 195 °C (468 K) for 6 hours.

The sheet samples were irradiated with a ps-laser and a fs-laser. The fourth harmonic wavelength of a Nd:YLF ps-laser (continuum; λ = 263 nm, τ = 8 ps, intensity = 1.5 mJ·pulse^{-1}, 10 Hz) was used for ablation in air. Fs-pulses were produced with a short-pulse KrF excimer laser system operating at 248 nm with τ = 500 fs [5, 6)]. The fs-laser irradiation was carried out in a vacuum chamber to avoid breakdown of air on the sample. The laser-ablated surfaces of the samples were analyzed by scanning electron microscopy (SEM; Topcon, DS-720). Because of their rather high electrical surface conductivity, these samples were not coated with an additional gold layer before SEM observation. The chemical compositions of the sample surfaces were also analyzed by X-ray photoelectron spectroscopy (XPS, Perkin Elmer, PHI5600ci) using monochromatic Al-Kα radiation.

Results and Discussion

Figure 1 shows SEM pictures of the surface after ps-laser irradiation (λ = 263 nm) at a fluence (F) of 500 mJ·cm^{-2}·pulse^{-1} (peak power (=F/τ): 62.5 GW·cm^{-2}·pulse^{-1}). The size of tip-like microstructures (4-8 μm) is smaller than that found in cases of ns-laser irradiation. Upon the ns-KrF excimer laser irradiation (λ = 248 nm) at 500 mJ·cm^{-2}·pulse^{-1} (peak power: 1.7 MW·cm^{-2}·pulse^{-1}) with 100 pulses, the size of tip-like microstructures was ca. 10-15 μm [4a)]. As the microstructures in our previous studies formed under same conditions



a b

Fig. 1. Top-view SEM micrographs of the surface of the composite after irradiation with the ps-laser with (a) 50, (b) 100 pulses at 500 mJ·cm^{-2}·pulse^{-1} (bar = 15.3 µm).

in terms of laser fluence and shots, the differences between the microstructures must be explained as being the results of differences in pulse duration.

Thermal diffusion length (L) is related to thermal diffusivity (D) and time (τ) [2)]

$$L \approx 2(D\tau)^{0.5} \tag{1}$$

Table 1 shows the thermal diffusion length for the acrylate polymer and carbon (graphite) at different laser pulse durations, based on *eq.* (1). If we assume a perfect mixing of the carbon particles (average size: 24 nm) within the acrylate polymer in our sample, the average distance between neighboring particles would be approximately 33 nm in the polymer matrix. Since, upon irradiation with the ns-laser, the diffusion length of the polymer was much larger than the distance between neighboring particles, the polymer matrix would be heated enough to accelerate carbon aggregation during the ns-laser pulse. However, the lower thermal diffusion length in the case of ps-laser irradiation resulted in a smaller microstructure due to a lower level of carbon aggregation.

It is worth noting that the threshold fluence of the composite sample was ca. 40 mJ·cm^{-2}·pulse^{-1} for ablation with the ps-laser irradiation, whereas the threshold fluence for the graphite was ca. 300 mJ·cm^{-2}·pulse^{-1}. Since the threshold fluence for conventional polymers having high absorption in the UV region is 50-30 mJ·cm^{-2}·pulse^{-1} [1, 3)], these results suggest that the carbon particles and aggregates on the surface behaved as a photon absorber decomposing polymer chains through thermal energy transfer.

A drastic change on the surface was observed upon fs-laser irradiation. Instead of the tip-like microstructures, a roughness appeared on the surface after fs-laser ablation at

550 mJ·cm^{-2}·pulse^{-1} (peak power: 1.1 TW·cm^{-2}·pulse^{-1}), as shown in Fig. 2. This domain structure can be ascribed to the original structure of internal high-order network structure of the sample (7). In higher fluence regions up to 1.9 J·cm^{-2}·pulse^{-1}, a similar roughness was produced on the surface. Moreover, there was only a negligible accumulation effect for the number of laser shots. The shape of the microstructure did not change with increases in the number of laser shots. These results indicate that this kind microstructure is due to the negligibly low thermal effects induced by fs-laser irradiation. Table 1 shows that the fs-regime had the lowest diffusion length in comparison with the other three time regimes. Carbon aggregation on a surface irradiated with a fs-laser would be suppressed when the photon energy is accumulated into the sample.

Table 1. Thermal diffusion lengths (*L*) of acrylate polymer and carbon at different times (τ).

τ	L	
	acrylate polymer [a)]	carbon (graphite) [b)]
30 ns	160 nm	3500 nm
8 ps	2.5 nm	56 nm
500 fs	0.63 nm	14 nm

[a)] *D* of acrylate polymer at RT: 0.002 cm^2·s^{-1}
[b)] *D* of graphite at RT: 1.0 cm^2·s^{-1}

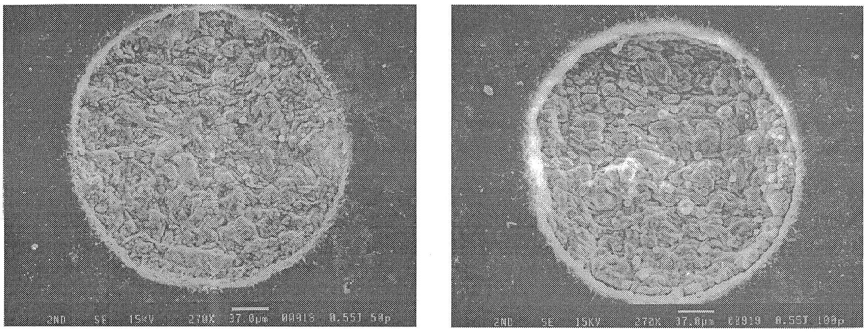


Fig. 2. Top-view SEM micrographs of the surface of the composite after irradiation with the fs-laser with (a) 50, (b) 100 pulses at 550 mJ·cm^{-2}·pulse^{-1} (bar = 37 μm)

Moreover, Küper and Stuke reported that polymethylmethacrylate (PMMA), whose single-photon absorption at 248 nm is negligible, showed higher absorption induced by 300 fs UV excimer laser irradiation at 248 nm, due mainly to non-linear absorption enhanced by the ultra-short laser irradiation (8). Upon fs-laser irradiation, the photo-absorption of the polyacrylate matrix in the composite would be increased. The unique shape of the microstructure formation would be caused by non-thermal effects and the non-linear absorption of the matrix polymer.

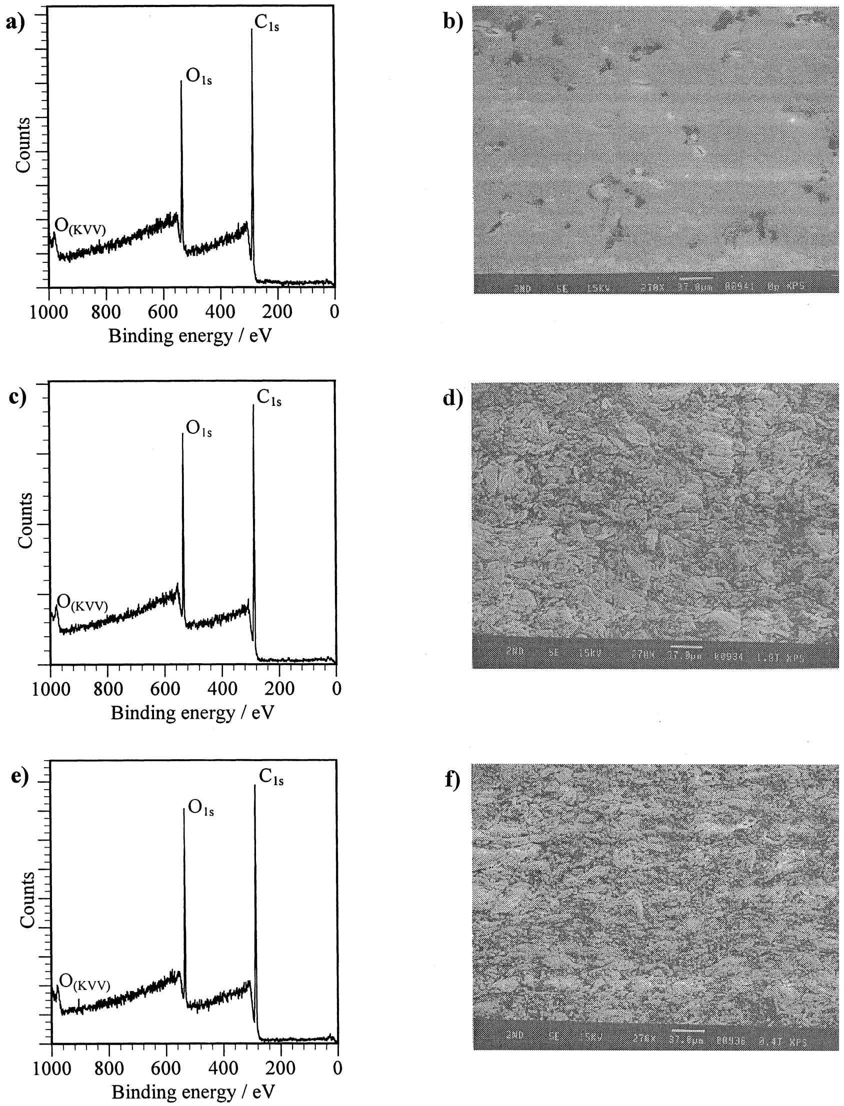


Fig. 3. XPS spectra (a, c, d) and SEM pictures (b, d, f) of the surface of the composite; (a, b) before laser irradiation, (c, d) after irradiation of the fs-laser at 1.9 J·cm^{-2}·pulse^{-1} with 9 pulses, (e, f) at 400 mJ·cm^{-2}·pulse^{-1} with 9 pulses (bar on SEM: 37 μm).

This assumption is supported by an XPS analysis of the surface. Figure 3 shows XPS spectra and SEM pictures of the sample surface before and after laser irradiation. Table 2 indicates that there was no significant difference in the atomic ratio of carbon and oxygen before and after fs-laser irradiation. This means that carbon aggregations on the irradiated area were suppressed under fs-laser ablation. Selection of an appropriate laser-pulse duration can regulate the thermal effects on ablated surfaces of the sample. These phenomena have also been observed in the case of metals 9), polymers 10, 11), glasses 12, 13), ionic crystals 14) and ceramics 15).

Table 2. The atomic ratio of carbon (C_{1s}) and oxygen (O_{1s}) before and after fs-laser irradiation (Atomic factor: $C_{1s} = 0.296$, $O_{1s} = 0.771$).

Laser irradiation	Atomic ratio (O_{1s} /C_{1s})
Before irradiation	0.25
1.9 J·cm^{-2}·pulse^{-1} (3.8 TW·cm^{-2}·pulse^{-1}) with 9 pulses	0.27
400 mJ·cm^{-2}·pulse^{-1} (0.8 TW·cm^{-2}·pulse^{-1}) with 9 pulses	0.28

Conclusion

The laser ablation of an elastomer composite was investigated using ultra-short pulses with fs- and ps-lasers. Intrinsic laser ablation without thermal effects was demonstrated in an experiment of fs-laser ablation of the composite, where the heat-affected zone on the surface during laser irradiation was negligible. These advantages of fs-lasers are very promising for various applications in precise material processing.

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