Excimer Laser Darkening of ETFE Polymer Films

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SYNOPSIS

Darkening of ethylene–tetrafluorethylene (ETFE) films caused by exposure to xenon chloride excimer laser radiation at 308 nm was studied. Darkening was determined to result from a rapid, local heating of the film. The laser-induced heating caused elimination of hydrogen fluoride from the film, leaving a noncrystalline graphitic backbone. A threshold laser fluence for darkening of (205 ± 25) mJ/cm^2 was observed. At laser fluences above this threshold, the rate of darkening of the ETFE films increased linearly with laser fluence. The rate of darkening was found to decrease as the extent of crosslinking in the polymer sample increased. Observations suggest that low concentrations of monomers in the film might affect the darkening rate.

INTRODUCTION

There has been considerable recent interest in the interaction of laser beams with polymers.[1-3] The light from pulsed UV lasers can efficiently and cleanly ablate many polymers, permitting either gross removal of material[4] or detailed micropatterning of polymers.[5] UV lasers can also interact with polymers by initiating chemical reactions in the irradiated regions.[6] These laser-induced reactions can locally change the physical properties of the polymer, and those changes can be utilized, for example, to mark polymers. In many cases, however, the chemical changes occurring in the polymers are not well understood.

The interaction of the copolymer ethylene–tetrafluoroethylene (ETFE) with UV lasers has been studied recently by Creasy and Brenna.[7] They studied ablation of ETFE with excitation at 266 nm by mass spectrometrically detecting the gas-phase ions produced. They observed that the laser/polymer interactions changed as the sample was exposed to more laser pulses. Near the threshold for ion production (100–300 mJ/cm^2), no products were observed for the first few laser pulses as the initially clear polymer film began to darken. After the sample had darkened, laser light was more efficiently absorbed at the surface of the polymer and ablation began. Carbon was ablated from the surface and gas-phase reactions of the ablated products yielded high-mass, even-carbon cluster ions (fullerenes) with the largest signal corresponding to C_{60}^+. This distribution of products was similar to those observed following the ablation of graphite. After 70 laser pulses on one spot, the high-mass fullerene–ion distribution was no longer observed, and ions with a lower mass distribution were observed with the largest peak assigned to $C_3H_3F_2^+$. The disappearance of the high-mass fullerene–ion distribution was attributed to a decrease in the ablation rate (as the absorption depth in the polymer decreased) resulting in a lower gas density of the ablation plume. Thus, the ejected ions underwent fewer gas-phase reactions.

In this work, we look more closely at the initial darkening of ETFE. We have concentrated on the changes that occur in the polymer during the pulses before ablation occurs. This regime is of particular importance for understanding laser marking of polymers, often achieved with a single laser pulse. This work on the marking of pure ETFE polymers provides useful information for assessing the marking of more complex systems. In polymers containing various additives, such as wire insulations, knowledge of the marking behavior of each component will help development of formulations that will op-

timize marking. The source of UV excitation in this work was an excimer laser operating at 308 nm. We have investigated the conditions required for darkening, the physical and chemical changes that occur during the darkening process, and the effect of crosslinking of the polymer on the darkening process.

EXPERIMENTAL

ETFE samples were irradiated with the output of a xenon chloride excimer laser (Lambda Physik EMG 201E) having a pulse width (FWHM) of 14 ns. A central, uniform portion of the beam was selected by a square aperture and then imaged with a lens onto the polymer film. For the fluence dependence, a 0.5 × 0.5-cm aperture was used and the emerging beam was imaged to an area of 0.021 cm² on the film. For the dependence on high-energy electron dose, a 1.0 × 1.0-cm aperture was imaged to an area of 0.13 cm². Dielectric coated beam splitters and quartz flats were used to attenuate the beam to vary the fluence. Laser energy was measured on every pulse with calibrated joulemeters (Gentec ED-200) looking at light reflected by a beam splitter placed in front of the sample. The beam from a 1-mW He–Ne laser (Spectra Physics) was focused with a telescope through the section of the film irradiated by the excimer laser. The size of the He–Ne beam through the sample was kept less than 70% of the excimer laser spot. The He–Ne laser beam transmitted through the ETFE sample was detected by a Si photodiode (Newport 882) and the photodiode signal, terminated into 600Ω, was recorded by an oscilloscope.

Raman spectra of ETFE samples were acquired with a triple spectrograph system (Instruments SA S3000) using 100-μm slits. An 80× microscope objective (Olympus) was coupled to the entrance slit. Excitation from an argon ion laser (20 mW, 514.5 nm) was focused onto the sample by the microscope and data was recorded at Raman shifts between 100 and 1,800 cm⁻¹. UV/visible absorption spectra were recorded on a Cary 17D spectrophotometer. Nd:YAG laser irradiations were performed with a Spectra Physics GCR-3/HG-2B laser system. The ETFE samples used in the laser fluence studies were 0.010-cm thick films of Tefzel® 2055 obtained from Du Pont. The ETFE used in the studies of high-energy electron dose were 1- to 2-mil thick Tefzel® 200 (in detail: film 150 ZM, no irradiation; 200 CLZ-20, 9 Mrad; 100 LZ, 19 Mrad and 29 Mrad). High-energy electron irradiations were performed in air.

RESULTS AND DISCUSSION

Physical Changes

Darkening of ETFE polymer films caused by irradiation with 308-nm light from a xenon chloride excimer laser was studied by measuring the transmission of a He–Ne laser beam through the film. UV/visible absorption spectra of the darkened areas showed a flat, unstructured absorption throughout the visible part of the spectrum. Thus, transmission measurements at the He–Ne laser wavelength of 632.8 nm are representative of the darkening of the film throughout the visible region.

Figure 1 shows the transmission of the He–Ne laser beam through an ETFE film as a function of number of excimer laser pulses for a number of different excimer laser fluences. At a laser fluence of 110 mJ/cm², no darkening occurred in clear ETFE films. Localized darkening, however, was observed after 20 shots at imperfections in the film where the film was not clear and increased absorption of the laser energy occured. At laser fluences above a threshold of 200 mJ/cm², darkening occurred throughout the laser-irradiated region of the ETFE film. As the first few laser pulses began to darken the film, the UV absorption cross-section of the film also increased. Thus, the energy deposited into the film per laser pulse increased as the film darkened. The rate of darkening increased until the supply of nonabsorbing molecules began to be depleted. After the films were extensively darkened, ablation of the darkened area was observed.
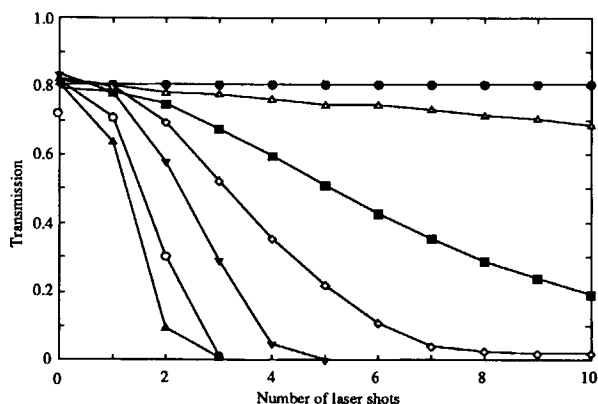
Figure 1 Transmission of ETFE films at 632.8 nm as a function of number of laser shots the sample had received from an XeCl excimer laser at 308 nm. The different data sets correspond to irradiation at different laser fluences (mJ/cm²). ●, 110; △, 220; ■, 360; ◇, 480; ▼, 570; ○, 710; ▲, 860.

Darkening of an ETFE film results from laser-induced chemical changes in the polymer, transforming species that are transparent in the visible spectrum to species that are highly absorbing throughout the visible spectrum. If we consider the visible transmission per unit length (neglecting reflective losses) to be determined by the absorption of n absorbing species all having an absorption cross-section σ, we can write the visible transmission of the film as:

$$T_{\text{vis}} = e^{-n\sigma}. \tag{1}$$

When the film is irradiated by the laser, the visible transmission changes as:

$$dT_{\text{vis}} = -\sigma e^{-n\sigma} dn. \tag{2}$$

If we assume that the darkening rate is proportional to the number of ultraviolet photons absorbed by the visibly transparent molecules when the laser fluence is above some threshold level, then the number of visibly absorbing species produced can be written as:

$$dn = \frac{\sigma_t \gamma}{\epsilon} (F - F_0) n_t. \tag{3}$$

In this expression, σ_t is the absorption cross-section of the visibly transparent molecule at the UV laser wavelength, n_t is the number of visibly transparent molecules irradiated by the laser beam, ϵ is the energy per laser photon, F is the laser fluence, F_0 is the threshold laser fluence below which darkening does not occur, and γ is the probability per photon absorbed that the darkening reaction will take place. This factor γ, similar to a quantum yield for reaction, may depend on laser fluence and on polymer properties such as the degree of crosslinking. If γ is constant as a function of laser fluence, then at fluences above the threshold the darkening rate will increase linearly with laser fluence, hence with energy deposited in the polymer. If we assume that above the threshold for darkening, γ is constant, and changes in n_t are small, then from eqs. (2) and (3), we see that the change of the visible transmission of the polymer film varies linearly with laser fluence.

In discussing the rate of darkening for pulsed laser marking of polymers, the time scale of interest is the number of laser pulses required to achieve a specified degree of darkening. One convenient measure of the darkening rate of the film is the inverse of the number of pulses needed to achieve a 50% reduction in transmission of the film, $N_{1/2}^{-1}$. Note

that a 50% reduction in transmission does not necessarily correspond to a 50% conversion of n_t to n. Values of $N_{1/2}$ for irradiation at different laser fluences were obtained from the transmission data. In Figure 2, $N_{1/2}^{-1}$ is plotted as a function of laser fluence. These data fall on a straight line, consistent with description of eqs. (2) and (3). Thus, at laser fluences above the threshold for darkening, the darkening rate increases linearly with laser fluence. This implies that γ is constant and the darkening "quantum yield" does not vary with fluence above the threshold. For fluences above 1000 mJ/cm^2, the ETFE films darkened too rapidly to obtain reliable values of $N_{1/2}$. Assuming no nonlinear behavior in the threshold region, we extrapolate a threshold laser fluence for darkening of (205 ± 25) mJ/cm^2 from a least-squares fit to the data in Figure 2.

Several observations indicate that the darkening of the ETFE is the result of a rapid, local heating process. First, the laser fluence threshold would not be observed in a purely photochemical process. Second, photon energy was not critical in darkening the ETFE. We observed darkening of ETFE films irradiated at 532 and 1064 nm with the output of a Q-switched Nd:YAG laser at 300 and 500 mJ/cm^2, respectively (these are not threshold values). When the 1064-nm beam was not Q-switched, the pulse energy (and the laser fluence) remained the same but the pulse width increased from 8 ns to approximately 200 μs. Using non-Q-switched excitation, no darkening of the polymer was observed. In the non-Q-switched case, the rate of local heating was not fast enough to overcome the dissipation of the
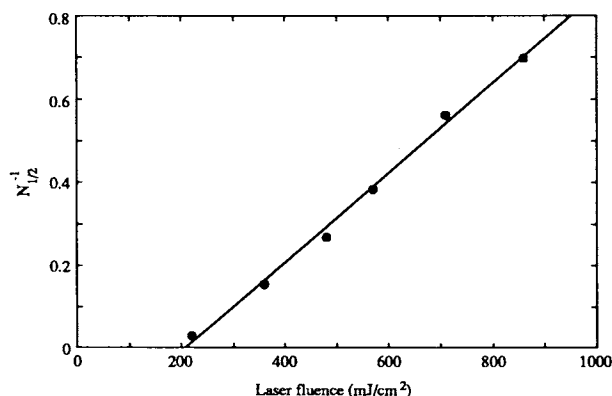
Figure 2 Inverse of the number of laser pulses required to achieve a 50% reduction in transmission, $N_{1/2}^{-1}$, plotted as a function of excimer laser fluence at the surface of the ETFE film. A least-squares fit to the data gives a threshold laser fluence required to achieve darkening of an ETFE film of (205 ± 25) mJ/cm^2.

deposited energy throughout the polymer during the laser pulse. As a result, the chemical reactions that result in darkening did not occur.

It should be kept in mind that laser power, rather than the typically reported laser fluence, may be the more critical parameter is assessing some laser/material interactions. However, in many cases, as long as the laser pulse width is much shorter that the time for energy dissipation, $\tau_{excitation} \ll \tau_{dissipation}$, small variations in laser pulse width will have little effect. In this context, since most excimer laser systems operate within a narrow range of pulse widths, comparison of laser fluences rather than laser powers is often justified.

In the initial stages of darkening, especially at low laser fluence, laser-induced changes occur in the polymer even though only a small amount of energy has been deposited in the film. In a 0.010-cm-thick ETFE film, a 308-nm laser beam passing through the film at a fluence of 300 mJ/cm^2 would heat the film by 5 K [using an 308-nm absorption coefficient (base 10) of 35 cm^{-1}, specific heat of 1.9 kJ kg^{-1} K^{-1}, and density = 1.7 g cm^{-3}].[8] Thus, rapid, localized internal heating of the polymer rather than bulk heating induced the observed chemical changes. These initial changes may not be readily visible, but their effects are cumulative. Film thickness may also affect the darkening rate as it will affect the depth profile of how energy is initially deposited in the film. As the film becomes darker, the absorption depth is greatly reduced and absorption takes place just at the surface of the film.
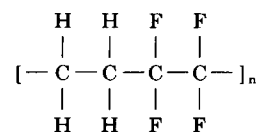
Chemical Changes

Chemical changes caused in ETFE by high-power excimer laser radiation were investigated by Raman microprobe spectroscopy. Figures 3(a) and (b) show Raman spectra of a non-laser-irradiated ETFE film and a similar film exposed to 6 pulses from a XeCl laser at a fluence of 300 mJ/cm^2. The non-laser-irradiated film shows a number of sharp lines that can be assigned to motions of groups in the ETFE polymer chain.[9] After six laser shots, those ETFE features are no longer observed and two broad features between 1,300 and 1,650 cm^{-1} dominate the spectrum. The two broad features in the spectrum grew and the ETFE peaks diminished in intensity as the sample was exposed to from one to six laser pulses. The two broad features have been assigned to amorphous or noncrystalline graphitic carbon.[10] Similar spectra were recently reported by Siperko et al.[11] following 266-nm laser ablation of ETFE.

The formation of graphitic carbon from an ETFE
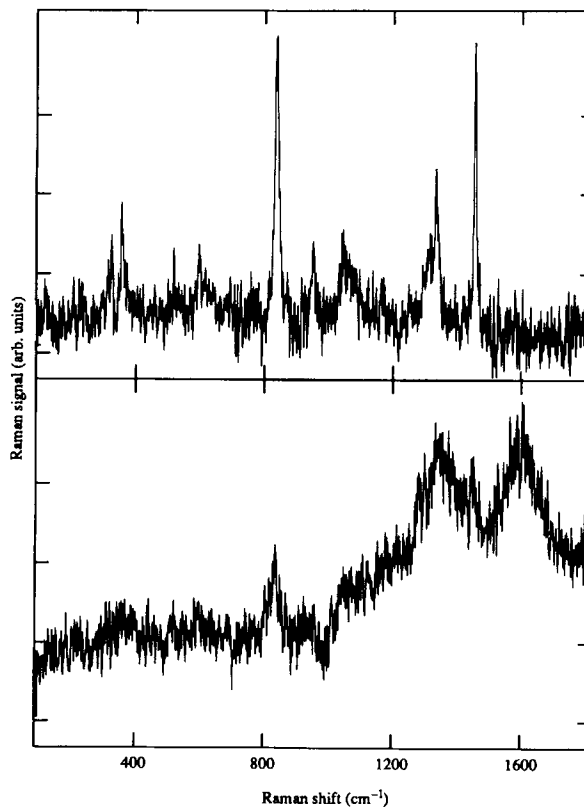
Figure 3 Raman microprobe spectra of ETFE films that were (a) not irradiated by the laser and (b) irradiated by six laser pulses at a fluence of 300 mJ/cm^2.

polymer requires the removal of hydrogen and fluorine atoms from the polymer chain. The structure of ETFE,

$$[-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}} - \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}} -]_n$$

suggests that hydrogen and fluorine can be removed from adjacent carbon atoms to eliminate an HF molecule. Concerted elimination of HF is more energetically favored than elimination of H$_2$ or F$_2$ (we estimate ΔH = 109, 137, and 685 kJ/mol, respectively, for HF, H$_2$, and F$_2$ elimination from the ΔH for elimination from CH$_3$CF$_3$, C$_2$H$_6$, and C$_2$F$_6$).[12,13] HF has been detected mass spectrometrically as a gas phase product of 308-nm excimer laser excitation of ETFE after exposure to two laser pulses (instrumental limitations prevented looking at the first pulse).[14] No evidence of F$_2$ elimination was observed and H$_2$ could not be detected in those experiments. We cannot conclusively differentiate between con-

certed HF elimination and the participation of step-wise radical chain reactions in these experiments. The ability to undergo HF elimination appears to be a major factor permitting the observed darkening of ETFE. Polyethylene and polytetrafluoroethylene, which could eliminate H_2 and F_2, respectively, but could not eliminate HF, were not darkened when they were irradiated under conditions that darkened ETFE. Thus, the experimental and thermodynamic data show that HF elimination rather than H_2 or F_2 removal is the major process involved in the transformation of the polymer backbone to graphitic carbon. Elimination of small hydrocarbon fragments may occur but would not play a major role in converting the backbone to a graphitic structure.

Evolution of HF from fluorine-containing polymers is well established.[15] However, thermal degradation of ETFE at temperatures in excess of 400°C proceeds by chain scission and exposure of the polymer to a flame does not char it. These observations indicate that under slow, thermal excitation the polymer degrades to low-molecular-weight fragments rather than leaving a graphitic skeleton.[16] Thus, laser darkening of ETFE proceeds by a different mechanism than conventional, slow thermal degradation.

The effect of polymer cross-linking on laser-induced darkening also provides information about the chemical processes that are occurring. ETFE polymers exposed to ionizing radiation form cross links between polymer chains.[16] The ETFE films used in this work that were exposed to high-energy electrons also became cloudy, an indication of increased crystallinity. The UV absorption of the films was not significantly affected by the ionizing radiation dose.
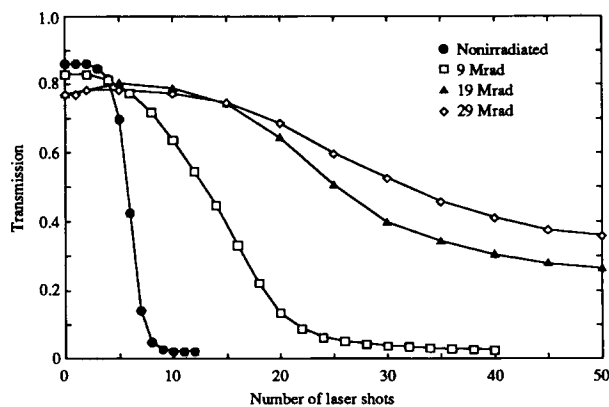
Figure 4 Visible transmission of ETFE films as a function of number of laser shots for films previously exposed to 0, 9, 19, and 29 Mrad doses of high-energy electrons. The laser fluence was 300 mJ/cm^2 in all cases.
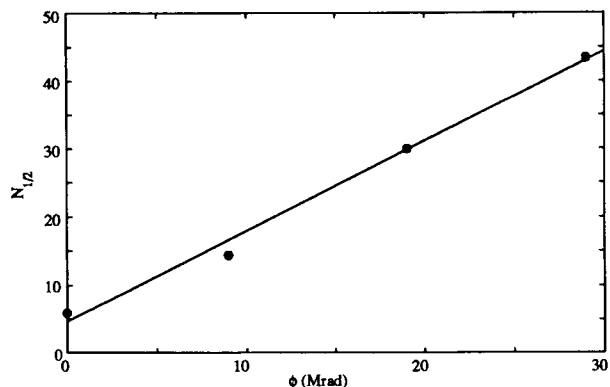

Figure 5 Number of laser shots required to achieve a 50% reduction in transmission, $N_{1/2}$, plotted as a function of ϕ, the dose of high-energy electrons to which the polymer was previously exposed. The solid line is a least-squares fit to the data.

Figure 4 shows the visible transmission as a function of number of excimer laser pulses for several ETFE films previously exposed to different doses of high-energy electrons. The laser fluence was 300 mJ/cm^2 in all cases. The rate of darkening of ETFE polymers decreased with increasing electron dose to which the sample was exposed. To examine the effect of ionizing radiation dose on the darkening rate, the data were fit to the expression:

$$N_{1/2}^{-1} = (N_{1/2}^0 + m\phi)^{-1}, \qquad (4)$$

where $N_{1/2}^0$ is the number of laser pulses required to achieve a 50% reduction in transmission for a sample that has not been exposed to ionizing radiation, m is a proportionality constant, and ϕ is the dose of ionizing radiation. Figure 5 shows that a plot of $N_{1/2}$ as a function of radiation dose is linear, that is, the number of pulses required to achieve 50% reduction in transmission increases linearly with sorbed radiation dose. Considering eqs. (2)–(4), the linear fit to the data in Figure 5 implies that γ, the probability per absorbed photon that the darkening reaction will occur, decreases with ionizing radiation dose to which the sample was exposed according to $\gamma \propto (N_{1/2}^0 + m\phi)^{-1}$. This conclusion can be reached because the laser fluence was constant for this set of experiments and the ionizing radiation dose did not significantly affect the initial UV absorption coefficient of the film. Crosslinking reduces the number of sites from which concerted HF elimination can occur and possibly inhibits chain reactions from propagating down the polymer chain. In addition, increased crystallinity may reduce the quantity of noncrystalline graphite that could be pro-
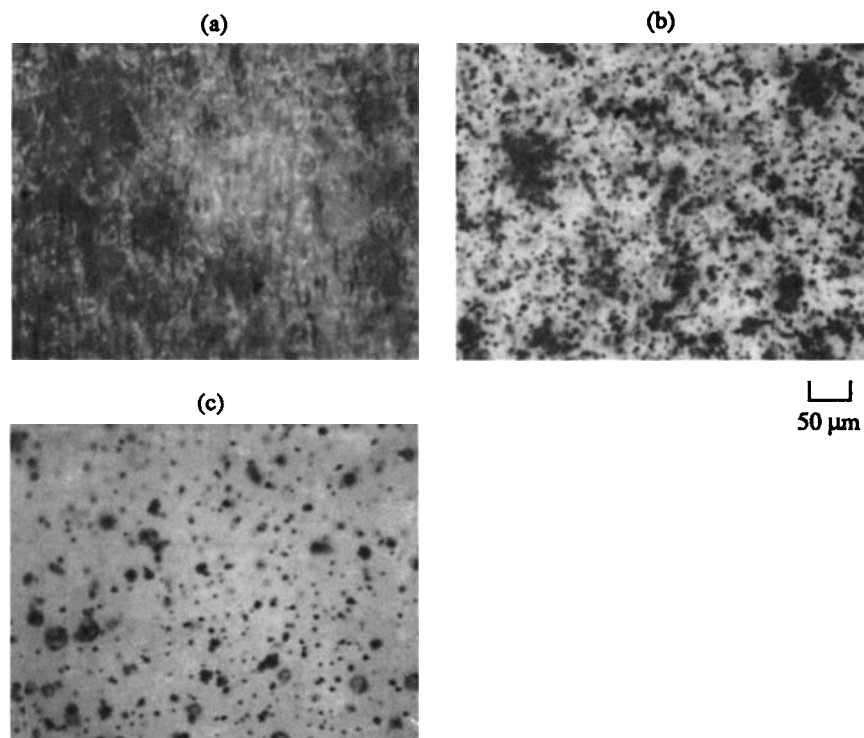
Figure 6   Optical micrographs of ETFE films exposed to 308-nm excimer laser excitation at 300 mJ/cm^2. (a), no high-energy electron dose, four laser shots; (b), 9 Mrad, 10 laser shots; (c), 29 Mrad, 20 laser shots.

duced if the laser did not break the crosslinks or reduce the crystallinity. However, on the samples exposed to the highest dose of radiation, an increase in transmission was observed following the first few laser pulses. This observation was interpreted as a loss of crystallinity resulting from the rapid heating and cooling initiated by the laser excitation.

The morphology of the marks obtained varied as a function of the high-energy electron dose. Figure 6 shows optical micrographs of the darkening obtained in samples that had been exposed to different radiation doses. The sample not exposed to high-energy electrons darkened after a few laser pulses and the darkening quickly spread from localized spots and filled the entire area of the film. With increasing radiation dose, more laser pulses were required to achieve comparable darkening; the darkening remained localized in discrete spots. Obviously, increased crosslinking prevents spreading of the darkening, perhaps by preventing sequential HF loss down the polymer chain.

A final observation regarding darkening rates is that the samples of Tefzel 200 required more laser pulses for darkening to begin than did the Tefzel 2055, which typically began to darken on the first

laser pulse (compare Fig. 1 sample at 360 mJ/cm^2 and the sample in Fig. 4 that was not exposed to high-energy electrons). The differences in chemical composition between the two samples is probably limited to only small changes in composition or concentration of minor monomer components.[17] Thus, these small concentrations of monomers may have large effects on the excimer laser marking of the ETFE films. For example, unsaturated monomers may be efficient absorbing species that act as sites for absorption and localized deposition of energy.

CONCLUSIONS

The physical and chemical processes in the darkening of ETFE polymers induced by high-power laser radiation have been characterized. The laser-induced darkening of ETFE proceeds by a rapid, local heating process. The major chemical process occurring is the elimination of HF from the polymer chains, leaving dark, noncrystalline graphitic material. With 308-nm excimer laser radiation in a 14-ns pulse, there is a laser fluence threshold of (205 ± 25) mJ/cm^2 for darkening to occur. The rate of

darkening increases linearly with laser fluence above the fluence threshold. Crosslinking of the ETFE by exposing the film to doses of high-energy electrons reduces the rate of darkening. Further studies to quantify the role of crosslink density and crystallinity on laser darkening would help provide a more detailed understanding of the structural changes that occur in that process. Different types of ETFE films were found to mark at different rates, suggesting that low concentrations of additives in the film might have a significant effect of the darkening rate. This observation may be significant in determining the optimum composition of a polymer to be marked by an excimer laser.

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