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INFRARED LASER DRIVEN DEGRADATION OF POLYTETRAFLUOROETHENE

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SUMMARY

CO<sub>2</sub> laser induced degradation of polytetrafluoroethene yields gaseous tetrafluoroethene, hexafluoropropene and octafluorocyclobutane along with solid polytetrafluoroethene deposited on reactor surface. All the products except octafluorocyclobutane are suggested to arise from primary cleavage of the polymer and the relative amounts depend on incident energy density of laser radiation and added gases. The characterization of solid deposit by scanning electron microscopy and adsorption measurements is presented.

INTRODUCTION

Conventional pyrolytic decomposition of polytetrafluoroethene (PTFE) affords tetrafluoroethene along with hexafluoropropene and octafluorocyclobutane [1-6]. The process suffers

from the involvement of hot vessel surface which makes the reaction less controllable and leads to unwanted side-products [7].

Laser-induced degradation of solid materials ensures surface-less conditions and gaseous products, being transparent to laser radiation, remain unexposed to high temperatures restricted to only irradiated area of the solid material. The interaction of PTFE with radiation of CO<sub>2</sub> lasers was studied until now only with regard to processing of the material [8-11] despite that different thermal conditions can also affect distribution of decomposition products. In this note we report on the PTFE degradation by infrared radiation of continuous-wave and pulsed CO<sub>2</sub> lasers which we examined in effort to find out whether specific local degradation of the polymer can lead to products different from those obtained in conventional pyrolyses.

#### EXPERIMENTAL

Experiments were carried out with three different CO<sub>2</sub> lasers, a tunable continuous-wave ([12], laser output 10-20 W) and pulsed TEA (0.9 J in pulse, repetition rate 2 Hz, pulse duration 150 ns fwhm, P. Hilendarski University Plovdiv) lasers both operating at the P(20) line of the 10.6 μm, and a technological continuous-wave (laser output 600-1500 W; Control Laser, Coventry) laser operating at 10.6 μm. The irradiation of both tunable CW and TEA lasers was focused with Ge and NaCl lenses. Different positioning of a PTFE target with respect to the lenses enabled to vary the incident energy density. The target (diameter 2.8 cm, thickness 2 cm) was housed in an evacuated 500 ml spherical flask equipped with NaCl window, a mercury manometer, a neck connecting it to a standard vacuum-line and with a side arm with a liquid nitrogen trap to freezing the condensable material after irradiation. Both flask and trap were furnished with a sleeve with rubber septum through which gaseous samples were withdrawn by a syringe after filling the set-up by helium and then injected into the mass spectrometer (GC-MS Shimadzu, model QP 1000, 2.5 m long

column with Porapak S or silicon elastomer OV-17, programmed temperature 100-200°C and 0-150°C, respectively). For the identification of products both retention times and mass spectra were compared to those of authentic samples. Quantities of gaseous products were estimated by mass fragmentography using  $C_2F_4$ ,  $CF_3CF_2$  and  $c-C_4F_8$  as standards.

Sulfur hexafluoride, 2-butene (both Fluka), hexafluoropropene (Matheson), carbon dioxide (Technoplyn) and polytetrafluoroethylene (du Pont de Nemours) were commercial samples and tetrafluoroethene was prepared as described in [1].

Scanning electron microscopy of PTFE deposit was performed on a Tesla BS microscope. IR spectra of the deposit were measured on IR Specord 75, Zeiss spectrometer.

Physical adsorption measurements were performed on a volumetric instrument DigiSorb 2600 (Micromeritics).

## RESULTS AND DISCUSSION

CW  $CO_2$  laser driven decomposition of PTFE yields gaseous tetrafluoroethene, hexafluoropropene and octafluorocyclobutane as well as solid polytetrafluoroethene deposited on the surface throughout the reactor as a fine powder. The relative amounts of these products are not affected by irradiation time, but depend on the density of the incident energy. The yield of PTFE powder ranges from 3 - 15 percent and that of tetrafluoroethene depends on the addition of gases (Table 1). Yield of tetrafluoroethene increases at the expense of octafluorocyclobutane upon the addition of nitrogen, sulfur hexafluoride and 2-butene. Total amount of gaseous products increases, however, only in the presence of  $SF_6$  and it decreases in the presence of nitrogen and 2-butene. The latter do not absorb the  $CO_2$  laser radiation and cannot thus directly increase their energy. Sulfur hexafluoride is, however, an excellent absorber of the radiation and can be heated [13] within the region of laser beam to temperatures higher than 1000°C. Faster degradation of PTFE in the presence of  $SF_6$  can thus be attributed to a hot gas-phase zone near irradiated polymer surface. Lower amounts of octafluorocyclobutane produced in the presence of all three

TABLE 1

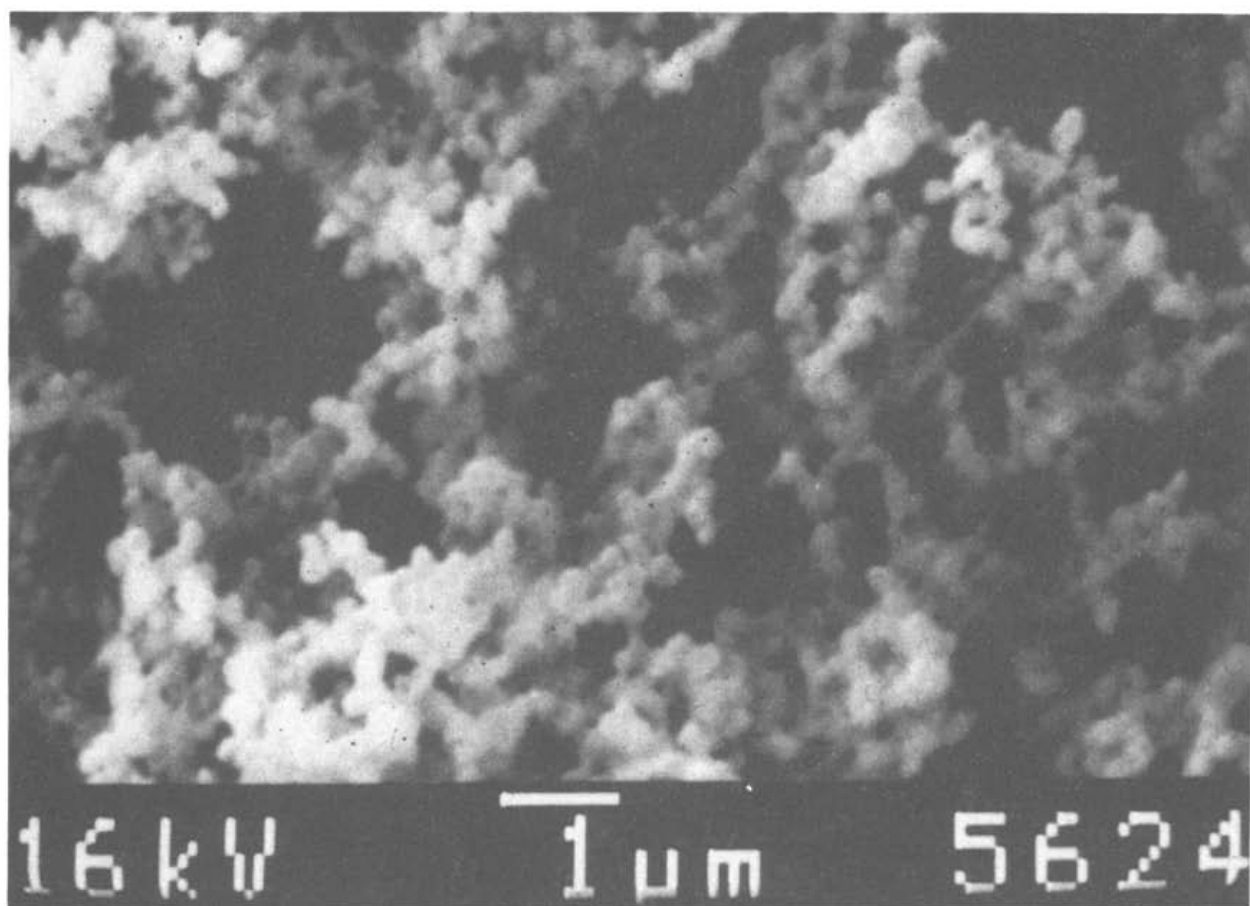
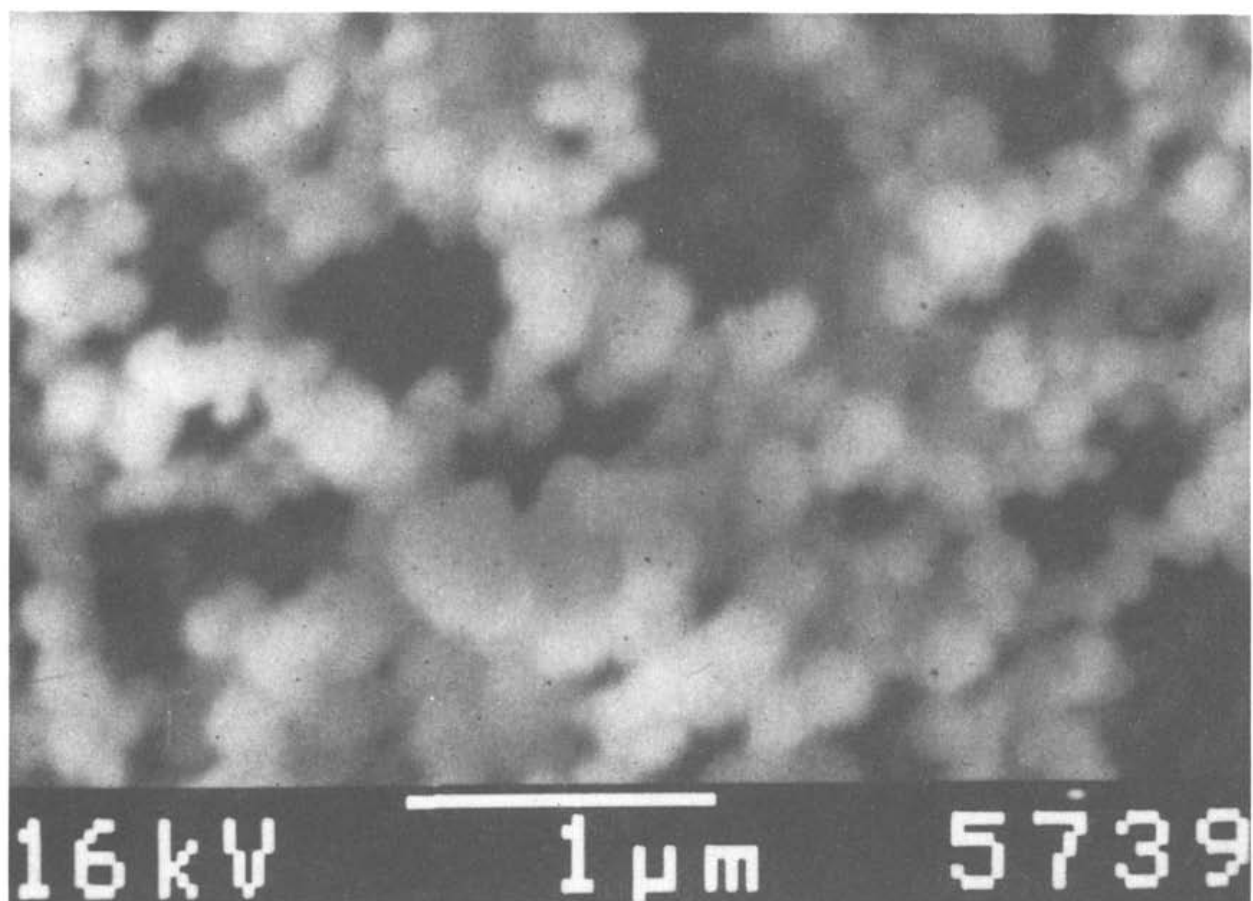
Continuous-wave CO<sub>2</sub> laser-driven degradation of PTFE

Laser output (W)	Incident energy density (W.cm <sup>-2</sup> )	Irradiation time (s)	Added gas, (Mbar)	total amount ( $\mu$ mol)	Gaseous products			
					C <sub>2</sub> F <sub>4</sub>	CF <sub>3</sub> CF:CF <sub>2</sub>	C-C <sub>4</sub> F <sub>8</sub>	molar percent of
10	5	180	-	61	56	16	28	
10	5	180	2-butene, 133	40	75	18	7	
10	5	15	SF <sub>6</sub> , 2.7	54	97	3	0	
20	10	50	-	81	57	16	27	
20	10	50	N <sub>2</sub> , 133	32	72	20	8	
15	30	30	-	78	76	14	10	
15	76	20	-	48	83	13	4	
15	480	20	-	41	87	13	0	
20	610	50	-	73	90	10	0	

TABLE 2

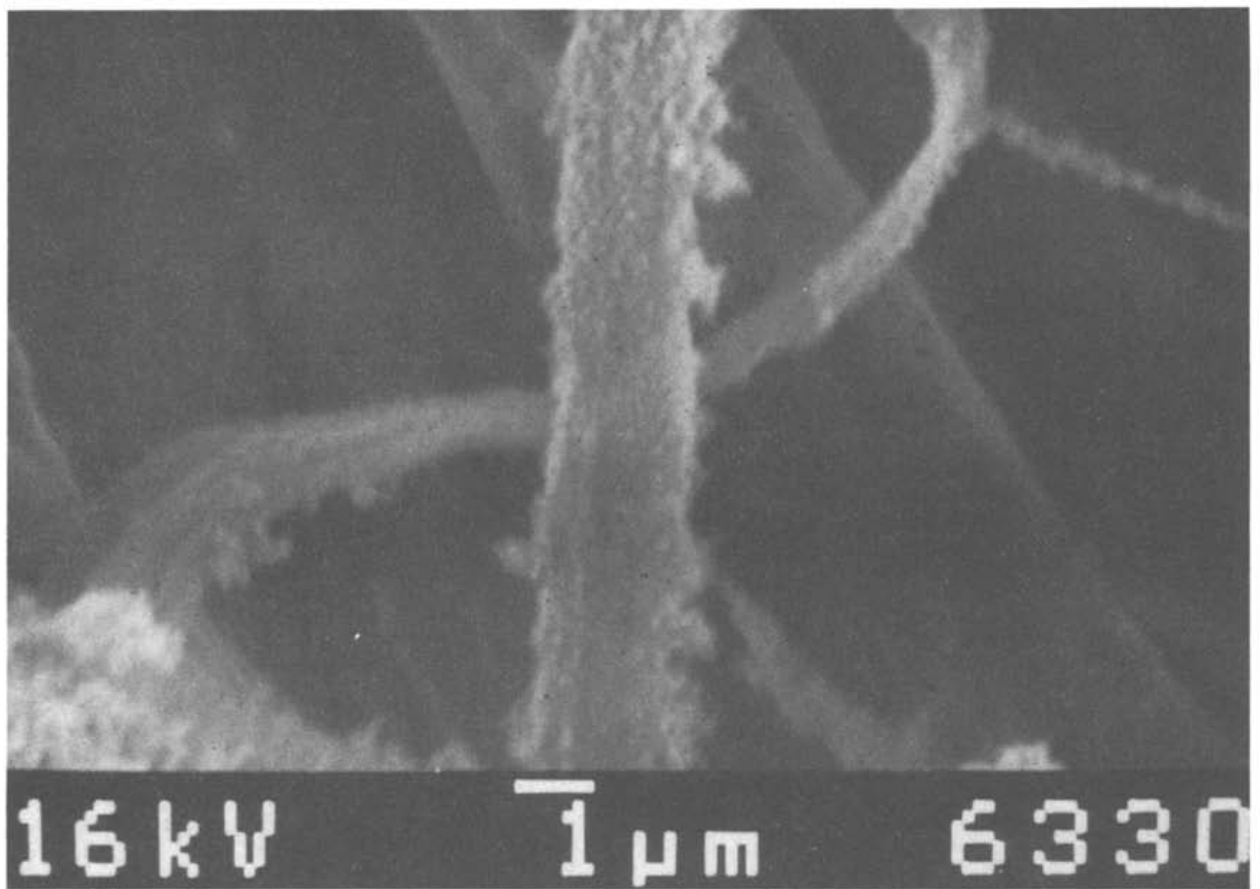
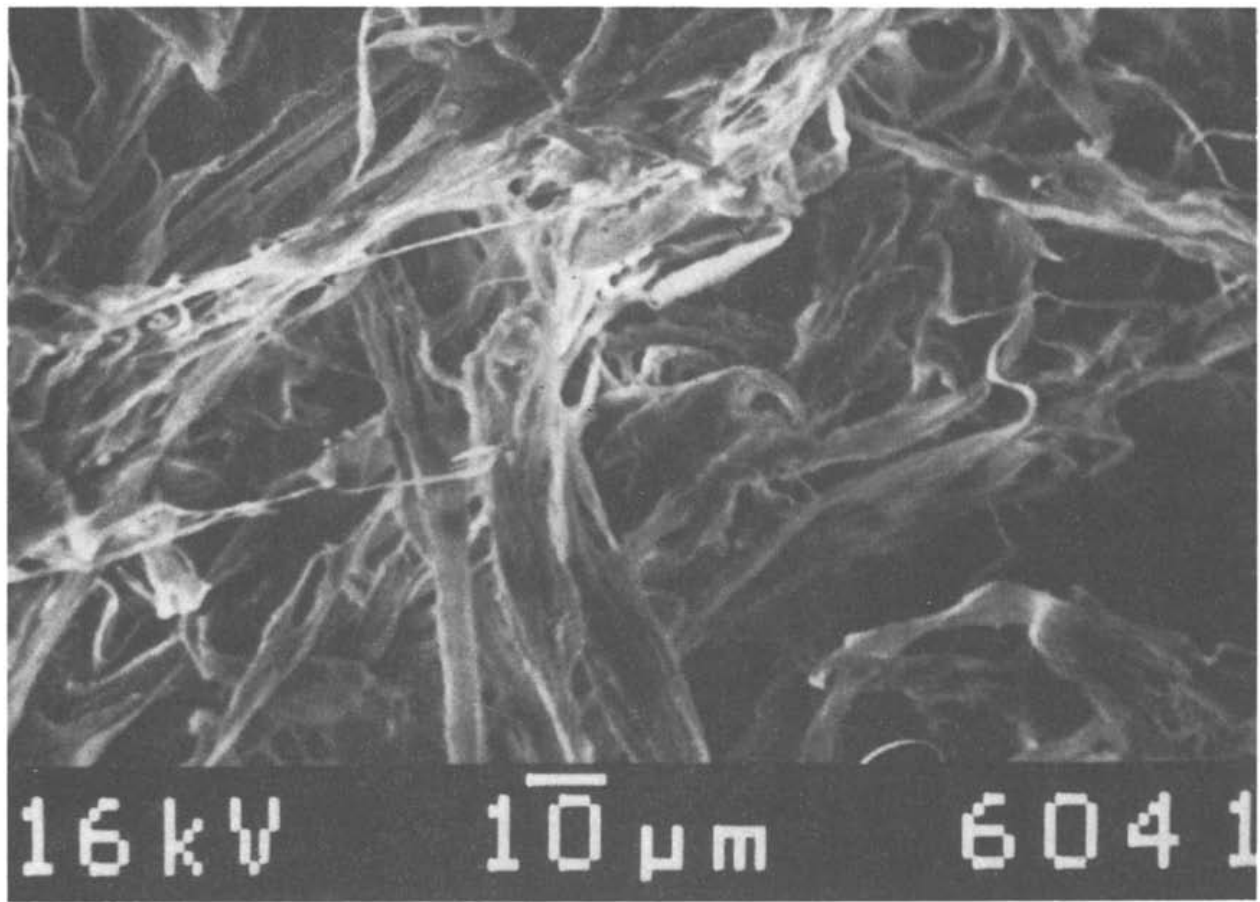
TEA CO<sub>2</sub> laser-driven decomposition of PTFE

Energy fluence (J.cm <sup>-2</sup> )	No. of pulses	Added gas (mbar)	Gaseous products	
			total amount (μmol)	molar percent of
			C <sub>2</sub> F <sub>4</sub>	CF <sub>3</sub> -CF=CF <sub>2</sub>
4	1000	CO <sub>2</sub> , 133	9	91
10	200	-	14	98
15	140	2-butene, 133	6	97
160	3	-	7	99



(a)

Fig. 1. SEM of PTFE deposit obtained with energy density  $5-480 \text{ W.cm}^{-2}$  (a) and  $610-1500 \text{ W.cm}^{-2}$  (b).



(b)

gases apparently relate to decreased ability of energized  $C_2F_4$  molecules propelled from the polymer to cycloadd to  $c-C_4F_8$  due to dilution by these gases. This assumption is in line with the fact that addition of fluoroethenes across double bond usually demands not only high temperatures but also higher pressures [14,15]. Tetrafluoroethene, hexafluoropropene and solid particles are probably the primary products of cleavage of PTFE polymer and they do not arise later in the gas-phase. Cleavage of PTFE into difluorocarbene does not seem probable. This species is known [14,15] to react with olefins like 2-butene to form three-membered rings, but no products of this reaction were detected. Hexafluoropropene can thus be assumed to arise from  $\cdot CF_2CF_2CF_2\cdot$  biradical by 1,2-rearrangement of fluorine.

TEA  $CO_2$  laser-driven decomposition of PTFE yields PTFE powder along with a mixture of tetrafluoroethene and hexafluoropropene, wherein the former strongly prevails. No octafluorocyclobutane is formed (Table 2). A decrease in the total amount of gaseous products in the presence of added gases resembles that in the cw- $CO_2$  laser induced degradation and is apparently associated with cooling ability of added gases.

The deposited white powder has typical absorption of an isolated  $CF_2$  group (wavelength/absorptivity:  $1155\text{ cm}^{-1}/36\%$ ,  $1225\text{ cm}^{-1}/48\%$ ) and its structure depends on the incident density of the energy of laser radiation. Scanning electron microscopy reveals that the deposit produced with the energy density  $5\text{--}480\text{ W}\cdot\text{cm}^{-2}$  consists of spherical particles ( $0.1\text{--}0.5\ \mu\text{m}$  in size) that are weakly bonded into movable aggregates (Fig. 1a) and that the deposit obtained by using the energy density  $610\text{--}1500\text{ W}\cdot\text{cm}^{-2}$  is formed by compact fibers covered with very tiny (less or equal  $0.1\ \mu\text{m}$  in size) particles (Fig. 1b).

Physical adsorption of nitrogen resulted in adsorption isotherms of type IV (BET classification) with no hysteresis loop. This indicates that the PTFE powder particles are non-porous; from their BET specific surface ( $8\text{--}12\text{ m}^2\cdot\text{g}^{-1}$ ) particle diameters of about  $0.1\text{--}0.2\ \mu\text{m}$  can be estimated (assuming spherical shape and PTFE density  $2.2\text{ g}\cdot\text{cm}^{-3}$ ) in fair agreement with the results of scanning electron microscopy.



The described laser induced degradation of PTFE is interesting from the viewpoint of production of fine powder that has a narrow size distribution. Similar particulate PTFE can be also prepared by polymerization of tetrafluoroethene in the liquid phase containing anionic surfactants [15-19] or by exposing tetrafluoroethene solutions [20] or coagulated dispersion PTFE [21] to  $\gamma$ -radiation. Very good stretchability of materials extruded from such powders [16-18] and their use as lubricant, in preparation of electrophotographic polymer coatings [22], nonferrous metal sintering [23] and perhaps its potential suitability to other purposes in the future make the reported laser induced degradation of PTFE a promising technique, since it can utilize waste PTFE.

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