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Osaka Laboratory for Radiation Chemistry

日本原子力研究所
Japan Atomic Energy Research Institute

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Osaka Laboratory for Radiation Chemistry
Takasaki Radiation Chemistry Research Establishment
Japan Atomic Energy Research Institute
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The annual research activities of Osaka Laboratory for Radiation Chemistry, JAERI during the fiscal year of 1992 (April 1, 1992 - March 31, 1993) are described.

The research activities were conducted under the two research programs: the study on laser-induced organic chemical reactions and the study on basic radiation technology for functional materials. Detailed descriptions of the activities are presented in the following subjects: laser-induced organic synthesis, modification of polymer surface by laser irradiation, radiation-induced polymerization, preparation of fine particles by gamma ray irradiation, and electron beam dosimetry. The operation report of the irradiation facilities is also included.

Keywords: Excimer Laser, Electron Beam, γ-Ray, Photochemical Reaction, Polymer Modification, Polymerization, Dosimetry

日本原子力研究所大阪支所年報（No.26）
1992年4月1日－1993年3月31日

日本原子力研究所高崎研究所
大阪支所

（1994年1月21日受理）

本報告書は，大阪支所において平成4年度に行われた研究活動を述べたものである。主な研究題目は，レーザー光による有機合成，レーザー光による高分子表面改質，電子線照射による重合反応の研究，γ線照射による微粒子の生成に関する研究および線量測定等である。

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Contents

1. Introduction

The annual research activities of Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, during the period of April 1992 - March 1993, are presented in this report.

The research activities were conducted under the following two research programs:

Study on Laser-induced Organic Chemical Reactions, and

Study on Basic Radiation Technology for Functional Materials

with the support of Operation and Maintenance Group of the irradiation facilities. The total number of people working in the laboratory was 25 including visiting research collaborator from industrial companies and research students from universities. JAERI funded expenditures during the period amounted to about 110 million yen, excluding personnel expenses.

The study on laser-induced organic chemical reactions was initiated in 1988 as an advanced frontier subject to utilize lasers to chemistry. Under this program, studies were carried out on (1) laser-induced chemical transformation of maleic acid to hydroxy acids as more valuable compounds and (2) surface chemical reactions induced by laser irradiation of fluorine polymers and sulfur containing aromatic polymers. Based on the fundamental study of surface reactions, investigations were extensively made to develope effective methods for the improvement of adhesive property and wettability on the surface of some fluoropolymers.

Concerning the research program of the basic study on radiation technology for functional materials, studies were carried out on (1) polymerization of spin casted epoxy film to obtain thin insulating film and preparation of self-organized monomolecular film for future molecular functional device, (2) preparation of ultra-fine metallic particles having catalytic functions and (3) low energy electron beam dosimetry.

In the operation and maintenance of the irradiation facilities, the cobalt gamma ray source and the Van de Graaff accelerator of 2 MeV were operated without any serious trouble for the irradiation. However, the operation of an accelerator of rectifier transformer type of 800 keV had to be interrupted due to the electric insulation failure of a cable. A new oil filled cable was installed in the accelerator and some modification and improvement of the facility were made.

Cooperate research programs with universities were carried out with 8 groups, while joint research programs with industrial companies were carried out under 3 subjects.

Irradiation service has been extended to the request of the researchers outside of the laboratory since April 1991. This year, 30% of beam time was used for this purpose.

A training program which is offered for scientists and engineers from industries has been carried out once a year since 1968. This seven day program includes lectures and laboratory experiences concerned with the radiation chemistry of polymers. We accepted 12 trainees this year. A seminar was offered to local citizens to give them basic knowledge on nuclear power and radiation. About 80 citizenes joined this one day seminar.

Detailed descriptions of the activities are given in Chapter 2. The list of the publications is given in Chapter 3, and the cooperative studies are summarized in Chapter 4.

Dr. Masafumi Nakano, Director
Osaka Laboratory for Radiation Chemistry

II. Current Research Activities

1. Laser-induced Photochemical Reaction of Maleic Acid in the Presence of Hydrogen Peroxide

Y. Shimizu, S. Kawanishi, M. Nishii, S. Sugimoto, and N. Suzuki

We have attempted to synthesize directly oxy acid, present-day mainly produced by very complex synthetic methods,[1, 2] from the irradiation of maleic acid aqueous solutions in the presence of hydrogen peroxide with XeF laser beams.

The N_2-saturated aqueous solutions of maleic acid (2H), monosodium (Na), disodium (2Na), and calcium (Ca) maleates (20 mM) were irradiated with the XeF laser (wavelength: 351 nm, pule energy: 80 mJ/pulse, intensity of photons: 1.41×10^{17} photons/pulse, frequency: 16 Hz, beam shape: 6×30 mm) at room temperature, and the aqueous 30% H_2O_2 was added to the solution at feeding rate of 3.4 ~24.6 ml/h. Analysis of products was carried out using ion chromatography (Yokogawa IC-100).

When the N_2-saturated maleic acid aqueous solution alone was irradiated in the absence of hydrogen peroxide, organic products were hardly produced.

Figure 1 shows the quantities of main products by the laser irradiation of 2H as a function of irradiation time at H_2O_2 feeding rate of 13.1 ml/h. As shown, glycolic acid was produced as a major product together with fumaric, oxalic, tartaric, succinic, and malic acids. The quantities of these products increased with irradiation time at early stage. The selectivities of glycolic, fumaric, oxalic, tartaric, and malic acids were 71, 12, 7, 4, and 2%, respectively. The combined selectivity of oxy acid (glycolic, tartaric, and malic acids) was 77%. These results indicate that oxy acid is directly and selectively synthesized by XeF-laser irradiation of N_2-saturated maleic acid aqueous solution in the presence of hydrogen peroxide.

Table 1 shows the effects of maleaes on the quantity of oxy acid. The XeF-laser irradiation of disodium and calcium maleates aqueous solutions increasingly enhanced the formations of tartaric and malic acids. The quantities of tartaric and malic acids were 3.8 and 2.5 times larger in the case of disodium maleates than in the case of maleic acid. The selectivities increased from 4 to 14% for tartaric acid, and from 2 to 9% for malic acid. The combined selectivity of oxy acid was 85%. Also, the quantities of tartaric and malic acids were much larger in the disodium and calcium maleates than in the maleic acid. On the other hand, the use of monosodium maleate hardly brought about the increment on the quantities of tartaric and malic acids. Thus, it was found that the formations of tartaric and malic acids were greatly enhanced when disodium and calcium maleates aqueous solutions were irradiated by the XeF laser. This finding suggests that the stability of the intermediates of maleates as ionic species is very important for the efficient formations of tartaric and malic acids.

References

1) "Chemicals of 10889, "(10889 No Kagaku Shohin in Japanese)" p.389, 1160, ed. by the Kagaku Kogyo Nippo Sha, Tokyo (1989).

2) H. Nohira, "Optically Active Substances, (Kogaku Kasseitai in Japanese)" p.27, Asakura, Tokyo (1989).

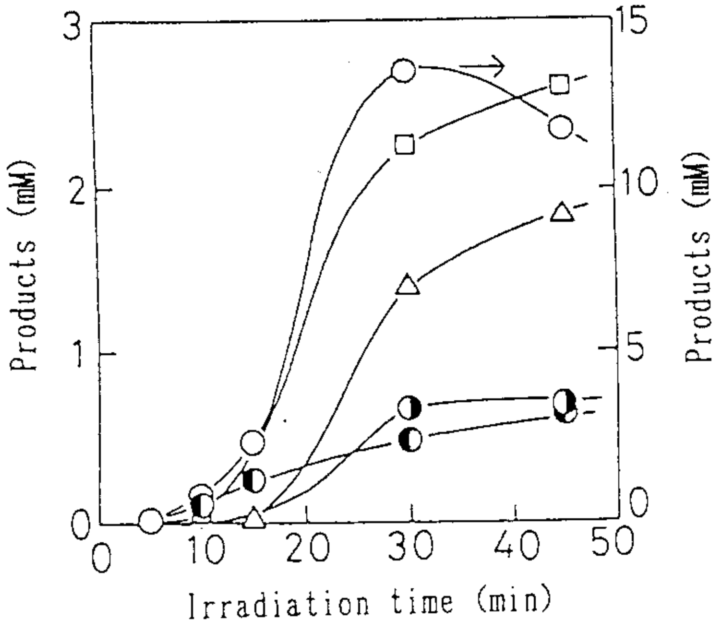

Fig. 1. Relationship between the quantities of main products with irradiation time. H_2O_2: 13.1 mℓ/h. ○:Glycolic acid, ○:Malic acid, ○:Tartaric acid, △:Oxalic acid, □:Fumaric acid.

Table 1. Effects of various maleates on the quantity of oxy acid [a]

Maleate	2H	Na	2Na	Ca
Tartaric acid	0.4	0.4	1.5	1.4
Malic acid	0.4	0.6	1.0	0.9
Glycolic acid	5.8	5.4	7.4	6.6

[a] Quantity: mM, Irradiation time: 45 min, H_2O_2: 3.4 mℓ/h.

2. Modification of Adhesive Property of Polytetrafluoroethylene by Excimer-laser Irradiation - Effect of blending of aromatic polymer and plasma treatment

M. Nishii, S. Sugimoto, Y. Shimizu, S. Kawanishi, N. Suzuki, T. Nagase,*
M. Endo,* and Y. Eguchi*

We have reported in previous report1) that the surface adhesive property of polytetrafluoroethylene (PTFE) film can be improved by KrF-laser irradiation in air when a small amount of aromatic polyester (APE) was blended with PTFE. In this study, the effect when the aromatic polymers such as polyetheretherketone (PEEK) and polyimide (PI) are blended in the PTFE was investigated.

The PTFE film (0.5 mm thick) was prepared using a peeling machine from the moldings of PTFE blended with PEEK or PI which were obtained by the sintering at 360 °C for 3 h. The surface adhesive property of irradiated PTFE film was evaluated by 180° peel strength of the film adhered on a stainless steel plate with the epoxy resin adhesive.

The peel strength was markedly improved by KrF or ArF laser irradiation of the PTFE film containing 1-15 wt% PEEK or PI with an increase in the content of these aromatic polymers. Figure 1 shows the peel strengths of the PTFE films irradiated by ArF or KrF laser, as a function of the laser-irradiation energy. Enhancement of the surface adhesive strength induced by ArF laser became more remarkable than that induced by KrF laser. From the change of XPS spectra of the PTFE films with laser irradiation, it was revealed that removal of F atom in $-CF_2-$ group, formation of carbonyl group, and carbonization occurred on the surface of PTFE. However, XPS spectral changes with ArF laser and KrF laser irradiations did not show pronounced difference. On the other hand, from the surface observation of the irradiated PTFE film by a SEM, fine unevenness with about 0.1 μm in diameter and rough deformation with about 1 μm in length were observed on the surface of the PTFE film irradiated by ArF laser. On the surface of the film irradiated by KrF laser, however, fine unevenness was merely observed. It is considered that morphological deformation of the surface of irradiated film contributes for the enhancement of the surface adhesive strength induced by ArF laser irradiation.

Surface modification of pure PTFE which is not contained UV absorbable substance such as aromatic polymer has been attempted. PTFE film (0.3 mm thick) was treated by plasma of glow discharge of H_2 and N_2 mixed gas, then the film was applied with UV absorbable solvent such as xylene and was irradiated by KrF laser beam in air. Surface of PTFE film became wettable for the solvent by the first plasma-treatment.

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* Technical Research Laboratory, Kurabo Industries, Ltd.

When pristine PTFE film was not treated with plasma, the adhesive property of the PTFE film did not improved by KrF laser irradiation (fluence: 300 mJ cm^{-2} $pulse^{-1}$, energy: 6.0 J cm^{-2}). However, the peel strength of the treated-PTFE film was increased remarkably from 0.01 kg cm^{-1} to 1.2 kg cm^{-1} with application of xylene and KrF laser irradiation of 0.6 J cm^{-2}. Figure 2 shows the peel strengths of PTFE films treated with various applied powers of plasma. This method is a significant one for the modification of PTFE, because it can be applied without to impair excellent mechanical, chemical, and electric properties of original PTFE.

Reference

1) JAERI-M 92-129, 27 (1992).

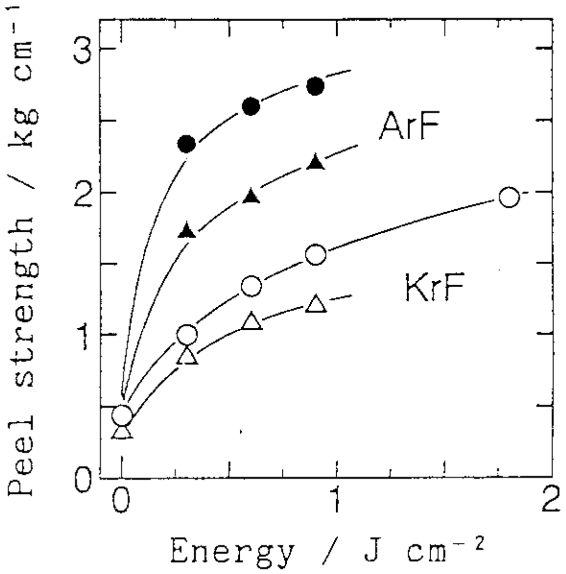

Fig. 1. Peel strength of the PTFE films containing aromatic polymer irradiated by ArF or KrF laser.
Content of aromatic polymer : 15 wt%.
Fluence : 150 mJ cm^{-2} pulse^{-1}.
(●, ▲)ArF ; (○, △)KrF ; (●, ○)PEEK ; (▲, △)PI.

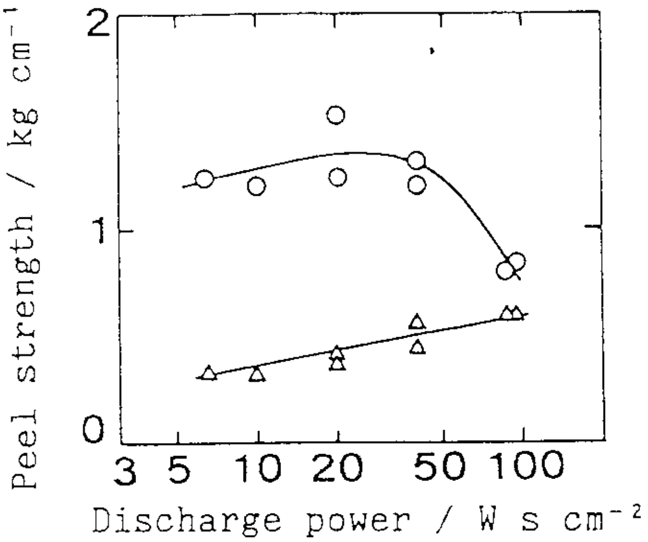

Fig. 2. Peel strength of the PTFE films treated by the plasma of H_2 and N_2 mixed gas and KrF laser.
Condition of RF glow discharge,
gas pressure : 0.1 Torr ; supplied RF power : 250 - 1,000 W
treated time : 8 - 24 sec
Condition of KrF-laser irradiation,
fluence : 300 mJ cm^{-2} pulse^{-1}; energy : 0.6 J cm^{-2}(2 shots)
(△)plasma-treated ; (○)plasma-treated then applied with xylene and laser-irradiated.

3. Modification of Wettability of PTFE Membrane with Excimer Laser Irradiation

T. Tanaka,* Y. Eguchi,* M. Nishii, S. Sugimoto, Y. Shimizu, and S. Kawanishi

PTFE membrane is excellent in thermal and chemical resistance, but poor in wettability. It is difficult to filter the aqueous chemicals directly with PTFE membrane. Therefore, new technique for surface modifying PTFE membrane is strongly expected. In this study, for giving wettability to the PTFE membrane without damaging its porous structures, we studied the modification of the PTFE membrane by using excimer laser.

The PTFE membrane was obtained from Japan Goretex. A pore size and a thickness of PTFE membrane were 0.1 μm and 45 μm, respectively. Critical surface tension of PTFE is 18.5 dyn cm^{-1}, and the wettability index of PTFE membrane was less than 31 dyn cm^{-1}. The membrane was impregnated with sodium silicate aqueous solution, and was irradiated with KrF or ArF excimer laser afloating on the sodium silicate aqueous solution at room temperature. The wettability of irradiated membrane was evaluated by the measurement of wettability index using the standard solutions with various surface tension.

Figure 1 shows the relationship between the fluence of laser and the wettability index of PTFE membrane irradiated by KrF excimer laser. Wettability index of the irradiated membrane increased with concentration of sodium silicate and at the fluence of 198 mJ cm^{-2} $pulse^{-1}$ became 44 dyn cm^{-1}. On the other hand, when it was not impregnated with sodium silicate aqueous solution, the index of the membrane irradiated in the same condition was less than 31 dyn cm^{-1}. It is considered that the wettability of the membrane was modified up to a level of polyethylene membrane (critical surface tension: 31 dyn cm^{-1}, wettability index: 41 dyn cm^{-1}) with excimer laser.

In the case of ArF excimer laser irradiation, wettability index which is similar to that one of KrF excimer laser irradiation was obtained, when the membrane was impregnated with more diluted solution of sodium silicate and irradiated at lower fluence than in the case of KrF excimer laser irradiation. Wettability index increased with decrease of the concentration of sodium silicate and became a maximum of 50 dyn cm^{-1} at 0.05%. Absorption coefficient at the wavelength of ArF was about a thousand as strong as that at the wavelength of KrF in the same concentration. For this reason, it is considered that irradiation with ArF excimer laser makes possible modification in more diluted solution than KrF excimer laser.

The changes in the chemical structure and the morphology on the surface of the membrane irradiated by KrF excimer laser were examined with XPS and SEM. Table 1 shows the atomic ratios, F/C and O/C, obtained from the peak areas of the C1s, F1s, and

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* Technical Research Laboratory, Kurabo Industries, Ltd.

O1s XPS spectra. In the irradiated membrane, the atomic ratio, F/C, decreased from 2.02 of unirradiated membrane to 1.69, and on the contrary, the atomic ratio, O/C, increased from 0.01 of unirradiated membrane to 0.08. It was made sure that surface porous structure of the membrane was not damaged by the irradiation process with SEM photograph. From these results, it is considered that this modification is not due to the change of morphology, but due to chemical reaction.

It was able to filter many chemicals directly without prewetting with alcohol by the PTFE membrane improved of wettability.

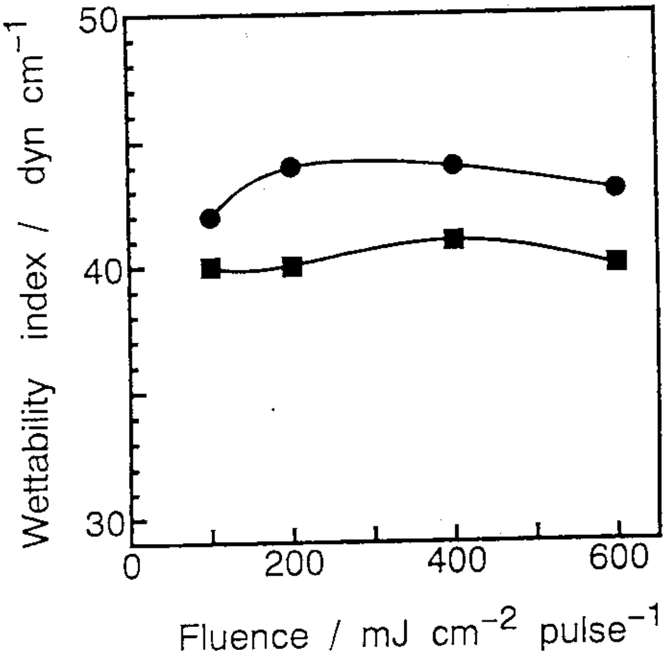

Fig. 1. Wettability index of PTFE membrane irradiated by KrF excimer laser.
Energy : 10 J cm^{-2},
Concentration of Na_2SiO_3 : 1%(●), 0.1%(■).

Table 1. Atomic ratios, O/C and F/C, of the surface of PTFE membrane irradiated by KrF excimer laser

	O/C	F/C
irradiated membrane	0.08	1.69
unirradiated membrane	0.01	2.02

Fluence : 198 mJ cm^{-2} pulse^{-1}
Concentration of Na_2SiO_3 : 0.1%

4. Effect of Dissolved Gases on the Surface Modification of Tetrafluoroethylene-perfluoroalkyl Vinyl Ether Copolymer by Excimer Laser Irradiation

A. Okada,* Y. Negishi,* Y. Shimizu, S. Sugimoto, M. Nishii, and S. Kawanishi

Perfluoropolymers are well-known for their excellent properties, for example heat resistance and solvent resistance. In addition, PFA has advantages of the molten processing. Therefore, the development of an effective method for the surface modification of PFA which is chemically inactive has become a very important subject for the enlargement of applications such as medical-use. The surface modification, for example endowment with the wettability and improvement of the adhesion, of PFA has been carried out by using an alkaline metallic solution[1)] and a plasma discharge,[2)] but we could not be satisfied completely with these effects. Therefore, we have attempted to proceed more efficiently the surface modification of PFA by ArF-laser irradiation in water which various gases was dissolved in.

The PFA film (0.1 mm thick) was prepared from the extrusion processing of PFA resin (Teflon PFA-350J Mitsui-Dupont Fluorochemical Co., Ltd.) and was cleaned in ethyl alcohol with a supersonic wave before irradiation. Then the PFA film was irradiated with an ArF laser (Lumonics Hyper EX-460, wave length: 193 mm, fluence: 12-95.8 mJ cm^{-2} $pulse^{-1}$, frequency: 10-50 Hz, number of pulses: 1870-16000 pulse) in distilled water which various gases was dissolved in. Respective gases was bubbled for 60 min at room temperature to be dissolved up to the saturated concentration (CO: 2.9×10^{-3} wt%, CO_2: 1.7×10^{-1} wt%, N_2: 1.9×10^{-3} wt%, O_2: 4.3×10^{-3} wt% at 20 °C).[3)] The quantity of light was determined by using a calorimeter (Scientech 38-4UV5). The wettability of the PFA film was evaluated from the contact angle towards water at room temperature. The chemical structure of the PFA film was analyzed by XPS (Shimadzu ESCA 850S) measurements.

The contact angle of non-irradiated PFA film was 106 degrees, however, the contact angle decreased remarkably to 34 degress by ArF-laser irradiation (energy: 208 J cm^{-2}) in water dissolved carbon monoxide. Also by irradiation in water dissolved carbon dioxide or nitrogen, the contact angle considerably decreased to 48 degrees or 70 degrees. On the other hand, no contact angle of the PFA film was changed by irradiation (energy: 208 J cm^{-2}) both in water dissolved oxygen or in air. Thus, it was revealed that the endowment with the wettability on the surface of the PFA film is influenced by the dissolved gases in water. We found that carbon monoxide dissolved in water takes an important role of the endowment with the wettability.

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* Shiga Laboratory, Gunze Ltd.

In the case of irradiation in water dissolved carbon monoxide, C1s XPS spectra of the PFA film show five peaks, which were newly assigned to -C=C- (285.5 eV), -C=O and -C-O-C- (288 eV), -COO (290 eV), -CF- (292 eV), together with -C-C- (285.5 eV) and -CF_2- (294 eV) observed on non-irradiated PFA. The peak area of the O1s XPS spectra increased, on the contrary, that of the F1s XPS spectra decreased by ArF-laser irradiation. These results suggest that the release of fluorine atom, the introduction of oxygen atom, and the formation of ethylene linkage occur on the surface of the PFA film by ArF-laser irradiation.

Figure 1 shows a correlation between the atomic ratios (F/C, O/C) and the contact angle on the surface of the PFA film. As you can see that, F/C decreased and O/C increased with the wettability enhanced. In the case of irradiation in water dissolved carbon monoxide, O/C became 4 times and F/C became 1/3 times compared to non-irradiated PFA. Therefore, these results indicate that the enhancement of the wettability, the release of fluorine atom, and the introduction of oxygen atom on the surface of the PFA film were closely related with each other.

It can be considered that the remarkable enhancement of the wettability of the PFA film by ArF-laser irradiation in water dissolved carbon monoxide is mainly attributable to the chemical effect described above. We are considering that the absorbed energy transfers from carbon monoxide to PFA, followed by the chemical reactions such as scission of the C-F bond at the interface between the PFA film and water.

References

1) E.R. Nelson, T.J. Kilduff, and A.A. Benderly, *Ind. Eng. Chem.*, **50**, 329 (1958).

2) H. Schonhorn and R.H. Hansen, *J. Appl. Polym. Sci.*, **11**, 1161 (1967).

3) "Kagaku Binran, Kiso" ed. by the Chemical Society of Japan, Maruzen, Tokyo (1984), Part II, p.158.

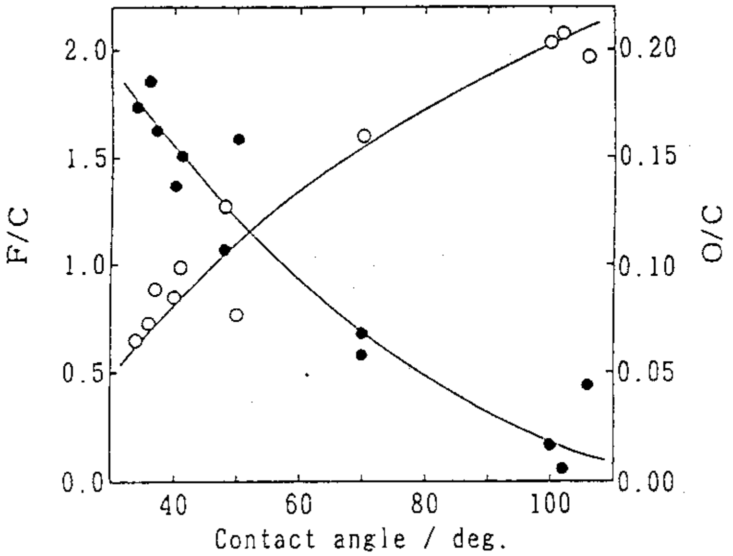

Fig. 1. Relationship between contact angle and ratios of atomic concentrations.
○: F/C, ●: O/C.

5. Photochemical Changes on the Surface of the Ethylene-tetrafluoroethylene Copolymer Film by Excimer Laser Radiation

Y. Hamada,* S. Kawanishi, M. Nishii, Y. Shimizu, S. Sugimoto,** K. Ema,*
and T. Yamamoto*

For about 20 years since the first excimer laser was invented, many studies dealing with the interaction of the excimer laser with solid organic materials were reported.1) In this period it has been obvious that excimer laser radiation is highly effective in modifying the surfaces of a variety of polymers.2) This method using excimer laser radiation is more efficient for modifying the polymer surfaces than several other ones in terms of (i) the modification at room temperature, (ii) the modification at short penetration depth, (iii) the microfabrication, and (iv) the modification of inert materials. Then recently, application of this method to the modification of the fluoropolymers is attempted.3)

In this study we picked up ethylene-tetrafluoroethylene copolymer (ETFE) from various fluoropolymers, for ETFE has higher absorbance in the UV-vis region than others. Using X-ray photoelectron spectroscopy (XPS), we investigated the chemical changes on the surface of ETFE irradiated with ArF and KrF lasers for the purpose of making it clear how the modification of the fluoropolymers was performed.

The ETFE used in this study was 50 μm thick film purchased from the Asahi Glass Co. Ltd. The chemical structure for the ETFE is shown in Fig. 1. The ETFE film was irradiated with ArF (193 nm) and KrF (248 nm) excimer lasers (Lumonics Hyper EX-460) having pulse widths of 10-12 ns and 12-15 ns for the ArF and KrF lasers, respectively. The laser irradiation was carried out in air at room temperature, and the frequency for operating laser was 1-10 Hz. The intensity of the laser was measured by a calorimeter (Scientech 38-4UV5). The XPS spectra were obtained with Shimadzu ESCA 850S using MgKα 1253.4 eV excitation (7 kV, 15mA) in vacuum (10^{-7} Pa). Under these experimental conditions, the Ag_{3d} level had a full width at half maximum of 0.8 eV.

Figure 2 shows C_{1s} XPS spectra of unirradiated ETFE (straight line) and that irradiated with the KrF laser with 106 J cm^{-2} (dashed line). The intensity of a peak attributed to the amorphous carbon (about 285 eV) increases instead of the decrease of those of two main peaks attributed to the -CF_2- group (about 293 eV) and the -CH_2- one (about 288 eV), and this attribution was determined by their binding energy. These changes in the C_{1s} spectra give the carbonization of ETFE induced by KrF-laser

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* Osaka University

** Radiation Application Development Association irradiation.

Figure 3 shows O_{1s} spectra of unirradiated ETFE (straight line) and the irradiated one (dashed line). KrF-laser irradiation on ETFE causes the increase of the intensity of the O_{1s} electron. This phenomenon indicates the oxidation on the surface of the ETFE film. On the other hand, the increase of the intensity at C_{1s} 290 eV in Fig. 2 suggests that the oxidation products were formed on the surface. From these results, the surface of the ETFE film is considered to be oxidized together with the carbonization.

As for ArF-laser irradiation the C_{1s} and O_{1s} XPS spectra provide the evidence that the oxidation products were formed on the surface of the ETFE film similar to the KrF one.

Considering no evidence of the oxidation induced with ArF- and KrF-laser irradiation in UV-vis spectra from the previous study4), the ETFE film is oxidized only on the surface. This phenomenon is supposed to result from the fact that the oxygen diffuses more at the surface of the ETFE film than at the bulk. Thus at the bulk of the ETFE film, the rate of the diffusion of the oxygen is expected to be much slower than those of the photochemical reactions induced by excimer laser irradiation.

References

1) For example, R. Srinivasan and W.J. Leigh, J. Am. Chem. Soc., 104, 6784 (1982).
2) R. Srinivasan and S. Lazare, Polymer, 26, 1297 (1985).
3) M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, T. Nagase, M. Endo and Y. Eguchi, Chem. Lett., 1992, 2089.
4) S. Kawanishi, Y. Shimizu, S. Sugimoto and N. Suzuki, Polymer, 32, 6 (1991).

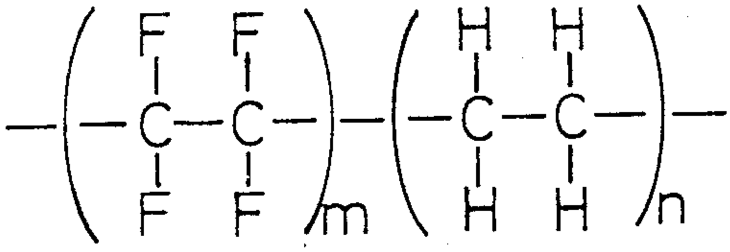

Fig.1 Chemical structure for ETFE

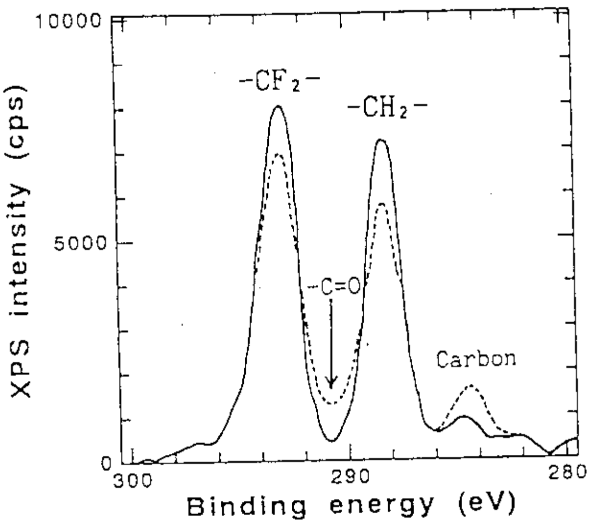

Fig.2 C_{1s} XPS spectra of unirradiated ETFE and ETFE irradiated with a KrF laser with 106 J•cm^{-2}

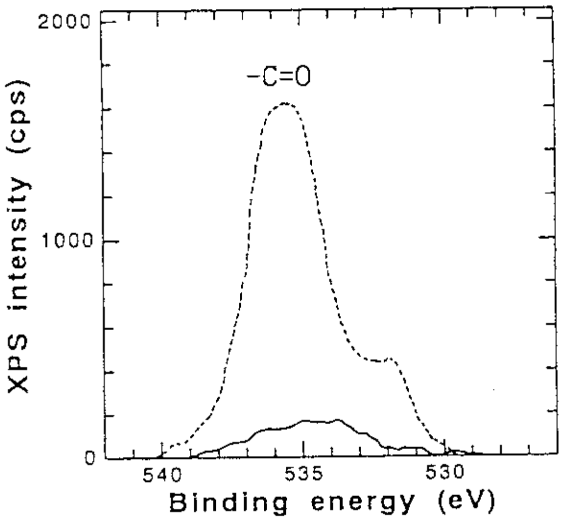

Fig.3 O_{1s} XPS spectra of unirradiated ETFE and ETFE irradiated with a KrF laser with 106 J•cm^{-2}

6. The Surface Chemical Reaction of Sulfur Containing Aromatic Polymer Irradiated by Excimer Laser

K. Ohnishi,* S. Arai,* S. Sugimoto,** M. Nishii, Y. Shimizu, S. Kawanishi and N. Suzuki

The surface chemical reaction induced by excimer laser irradiation of poly (ethersurfone) (PES) which are excellent engineering plastics has been studied.

After the surface of PES (100 μm thickness) was cleaned in ethanol with the supersonic wave for 10 min, the films were irradiated with ArF- (wavelength; 193 nm) or KrF- (248 nm) lasers in vacuo and in air at room temperature. The chemical change in the surface of the PES film irradiated with laser was measured using an X-ray photoelectron spectrometer (Shimadzu ESCA 850S) and a fourier transformation infrared spectrometer (Perkin Elmer, 1720X).

Figure 1 shows the change in O_{1s}, S_{2p} and C_{1s} XPS spectra on the surface of the PES film irradiated with the ArF-laser (8 J cm^{-2}) in vacuo. The intensities of the O_{1s} peak (532.5 eV, oxygen of sulfone group$^{1)}$) and S_{2p} peak (169 eV, sulfur of sulfone group) decreased remarkably by irradiation. At the same time, the new peak which is assigned to sulfur of sulfide group appeared at 164 eV. These results indicate that oxygen atom of sulfone group in the PES is released and sulfide group was formed by ArF-laser irradiation in vacuo. The cleavage of C-C and C-H bonds of aromatic ring in PES was very small in this condition.

Figure 2 shows the atomic ratios (O/C and S/C) on the surface of the PES film as a function of the irradiated energy in the case of ArF- and KrF-lasers irradiation in vacuo. About 36% of oxygen and about 25% of sulfur in the PES molecule are released by ArF laser irradiation of 8 J cm^{-2} in vacuo. In the case of KrF-laser irradiation, the O/C and S/C ratios decreased slightly with increasing the irradiation energy. Since the PES molecules has a strong absorption band at 200 nm$^{2)}$, ArF laser beam is absorbed more effectively into the PES molecule, compared with the case of KrF-laser beam. Large decreases in the O/C and S/C ratios by ArF-laser irradiation is attributed to the effective releases of oxygen and sulfur of sulfone group owing to more effective absorption of ArF-laser beam into the PES molecule.

Figure 3 shows the O/C and S/C ratios on the surface of the PES film as a function of the irradiation energy in the case of ArF- and KrF-lasers irradiation in air. In the case of ArF-laser irradiation, the O/C ratio hardly decreased in the irradiation energy range bellow 18 J cm^{-2}. The S/C ratio decreased remarkably with increasing the irradiated

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** Radiation Application Development Association energy and about 75% of sulfur in the PES molecule is released by irradiation of 18 J cm^{-2} in air. This indicates that the cleavage of C-S bond in the PES is enhanced remarkably by presence of oxygen.

In the case of KrF-laser irradiation in air, the O/C ratio increased with irradiated energy and about 41% of oxygen becomes incorporated into the PES molecule. The increased in the O/C ratio by KrF-laser irradiation in air is attributed to the increase of oxygen content in the PES molecule owing to the formation of carbonyl group. The formation of carbonyl group was confirmed by the appearance of the new C_{1s} peak at 289 eV of the PES film irradiated with the KrF-laser in air. This new peak is assigned to carbon of carbonyl group. Also, the formation of carbonyl group was ascertained by the analysis with an infrared spectroscopy at the 1700 cm^{-1} region. The S/C ratio decreased slight with increasing the irradiated energy. This indicates that the cleavage of C-S bond in the PES molecule by KrF-laser irradiation in air would be very small.

Conclusion: The irradiation effect of excimer laser beams on the PES film have been studied with XPS and FTIR. In the case of ArF-laser irradiation in vacuo, S=O and C-S bonds in the PES molecule were selectively cleaved to release oxygen atom, followed by the formation of sulfide group and sulfone group. In the case of irradiation in air, aromatic ring together with S=O and C-S bonds were cleaved remarkably to release of sulfone group and to form carbonyl group. The irradiation effects were much larger in ArF-laser irradiation than in KrF-laser one.

References

1) G. Marletta, S. Pignataro, A. Toth, I. Bertoti, T. Szekely and B. Keszler, Macromolecules, 24, 99 (1991).

2) H. Niino, M. Nakano, S. Nagano, A. Yabe and T. Miki, Appl. Phys. Lett., 55, 510 (1989).

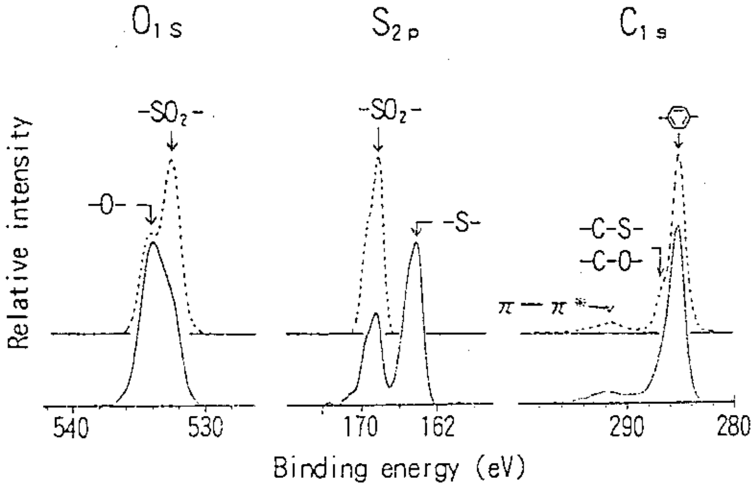

Fig. 1 XPS spectra on the surface of the PES film irradiated with the ArF laser in vacuo. -----: Without irradiation, ——: Irradiation of 8 J cm $^{-2}$. Fulence: 8 mJ cm $^{-2}$ pulse $^{-1}$.

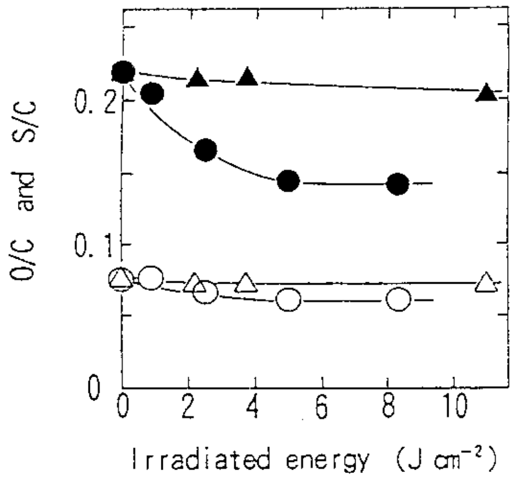

Fig. 2 O/C and S/C ratios on the surface of the PES film as a function of the irradiation energy in the case of ArF- and KrF- lasers irradiation in vacuo. ArF laser: O/C (●), S/C(○); KrF laser: O/C (▲), S/C(△). Fulence: 8 mJ cm $^{-2}$ pulse $^{-1}$ for ArF laser, 4mJ cm $^{-2}$ pulse $^{-1}$ for KrF laser.

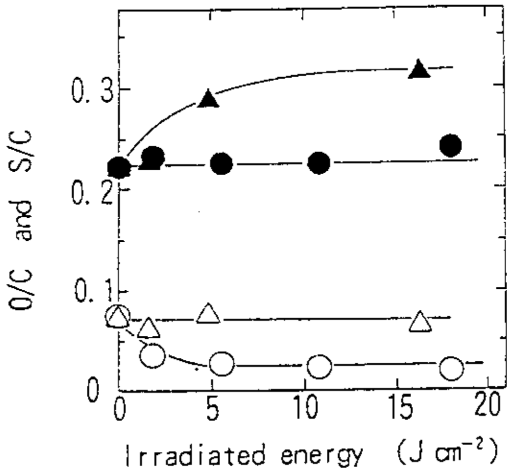

Fig. 3 O/C and S/C ratios on the surface of the PES film as a function of the irradiation energy in the case of ArF- and KrF- lasers irradiation in air. ArF laser: O/C (●), S/C(○);KrF laser: O/C (▲), S/C(△). Fulence: 18 mJ cm^{-2} pulse $^{-1}$ for ArF laser, 16 mJ cm $^{-2}$ pulser^{-1} for KrF laser.

7. Qualitative Changes in the Enamel by Excimer Laser Beams Irradiation: Comparison between Deciduous and Permanent Teeth

C. Miyazawa,* M. Kokubun,* S. Hamada,* T. Shimizu,* S. Sugimoto,**
Y. Shimizu, M. Nishii, S. Kawanishi and N. Suzuki

Effects of excimer laser irradiation on the CO_3^{2-} release and the F^- uptake were studied.

The F^- uptake of the enamel is largely dependent on the F^- concentration and the duration of the treatment but it is also affected by the crystallinity of the enamel. CO_3^{2-} is involved in the crystallinity, and its behaviors is related to F^- uptake[1, 2]. In apatite, the chemical bond of CO_3^{2-} is the weakest among all its constituents so that CO_3^{2-} is likely to be released first. Excimer laser[3], which produces short-pulse, high-output ultraviolet rays, photochemically cuts intermolecular bonds. We observed the behavior of CO_3^{2-} in the enamel after excimer laser irradiation and evaluated its effects on the F^- uptake and the acid resistance of the enamel.

The enamel was separated with a diamond cutter from extracted erupted deciduous teeth (deciduous teeth), completely erupted permanent teeth (permanent teeth), and completely impacted permanent teeth (impacted teeth) and ground to a particle size of 350-500 μm. About 300 mg of each sample was placed in a synthetic quartz tube (10 mmϕ), rotated, and irradiated by KrF excimer laser (248 nm, Lumonics Hyper EX-460). Irradiation was made at fluence and absorbed dose of 101.9 mJ cm^{-2} $pulse^{-1}$ and 100 J cm^{-2}. respectively (Irradiation I), or 203.0 mJ cm^{-2} $pulse^{-1}$ and 100 J cm^{-2} respectively (Irradiation II). Fluoridization was made by immersing 100 mg of the samples in NaF solution (100 ppm F^-, PH 7.0±0.1, 10 ml) for 1 month by exchanging the solution twice a week. F^- was assayed with ion electrode (Orion, Ionalizer/901) on the basis of McCann's method. CO_3^{2-} was assayed by Conway method, and Ca and P by ICP (Shimadzu, ICPS-50) luminescence analysis after wet incineration. The acid-tolerance test was made by shaking 10 mg of the sample in 10 ml of 0.4 M acetate buffer (PH 4.0) for 10 minutes and measuring the amount of Ca eluted by ICP. Differences in the mean value were examined by t-test.

The Ca and P contents and the Ca/P ratio in each sample showed no differences between Irradiation I and Irradiation II. Especially, the composition of the deciduous teeth was unchanged, indicating that laser irradiation caused no heat-induced degeneration such as carbonization. CO_3^{2-} in the enamel was reduced significantly (Probability: $p > 0.05$) in the deciduous teeth and permanent teeth after Irradiation I

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(Fig.1). CO_3^{2-} , the binding force of which is weakest among constituents of the enamel crystal, is considered to have been freed by the photochemical reaction induced by laser. The F^- uptake increased significantly ($p<0.01$ or $p<0.05$) in the deciduous teeth after Irradiation II (2,830 ppm) and in the impacted teeth after Irradiation I (2,050 ppm) as compared with the non-irradiated enamel (2,670 ppm in deciduous teeth and 1,840 ppm in impacted teeth). This increase in the F^- uptake indicates a close relationship between the decrease in CO_3^{2-} and laser irradiation2). Laser irradiation had no effect on the acid resistance of the enamel without fluoridization (Fig. 2). With fluoridization, however, the acid resistance was increased in the deciduous teeth after Irradiation I, in the permanent teeth after Irradiation II, and in the impacted teeth after Irradiation I and II. This increase in the acid resistance of enamel is considered to have been due to a reduction in CO_3^{2-} in the enamel crystal by excimer laser irradiation and a resultant increase in the F^- uptake.

Excimer laser irradiation reduced CO_3^{2-} in the enamel of deciduous and permanent teeth. Fluoridization of the irradiated enamel increased the F^- uptake and improved the acid resistance.

References

1) C. Miyazawa, M. Kokubun, M. Yuki, A. Kubota, and T. Shimizu, J. Dent. Hlth., 41, 486 (1991).
2) A. Kubota, Ohu Univ. Dent. J., 18, 191 (1991).
3) M. Maeda, "Laser Apparatus. Laser in Dental Medicine", T. Morioka, ed., Ishiyaku Publishers, 1986, p.19-38.

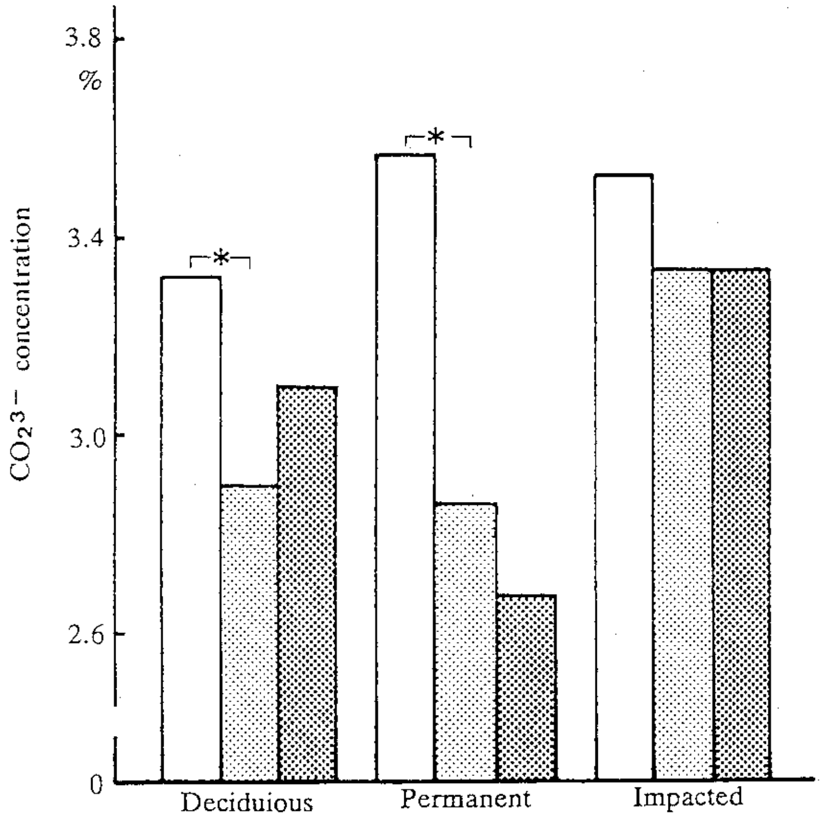

Fig. 1 The CO_3^{2-} concentration of excimer laser beam irradiated tooth enamel
□:Non-irradiation ░:Irradiation I ▓:Irradiation II
*:$p < 0.05$

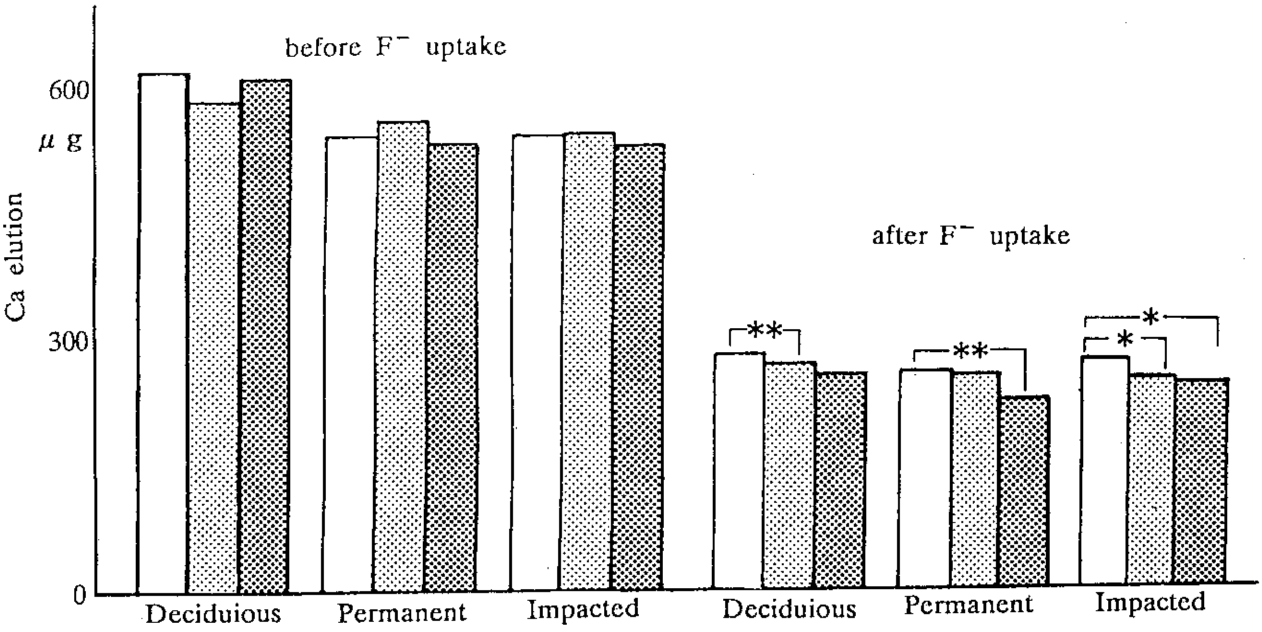

Fig. 2 The acid resistance before and after F^- uptake by excimer beam irradiated tooth enamel
□:Non-irradiation ░:Irradiation I ▓:Irradiation II
*:$p < 0.05$, **:$p < 0.01$

8. Influence of Excimer Laser Beams on Salivary α-amylase Activity

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S. Sugimoto,** Y. Shimizu, M. Nishii, S. Kawanishi and N. Suzuki

We examined the effects of an excimer laser irradiation on the activity of the human salivary α-amylase for treatment of caries teeth and to strengthen teeth surface enamel.

The solution of human salivary α-amylase 770IU/l (Kyokuto Seiyaku K.K.) was irradiated to 1,000 shots with the fluence of 17.3 mJ cm^{-2} $pulse^{-1}$ using a KrF excimer laser (248 nm).

We carried out the following analyses.

(1) Saccharification of starch; the saccharified zone (halo) by starch-iodine reaction after incubation at 37°C of laser-irradiated α-amylase immersed in a pulp disk on a starch-containing agar medium.

(2) α-Amylase activity; The α-amylase activity was measured by Kyokuto Amylase GA.

(3) Electrophoresis; The α-amylase solution irradiated with a laser beam was subjected to SDS-7.5% polyacrylamide gel electrophoresis.

Fig. 1 shows the results after the incubation for 48 hrs with application of 1,000 laser shots. With the increase in the number of laser shots, the saccharified zone became smaller in comparison with the non irradiated zone.

Fig. 2 shows the relationshop between the exposure of laser irradiation and the amylase activity. The amylase activity without laser irradiation (control) was 770IU/l and that after 1,000 shots was 300.86±14.35IU/l. This indicated that the activity of laser-irradiated amylase decreased with the increase in the number of laser shots.

Fig. 3 shows the results obtained by the electrophoresis of the amylase solution and a protein with a known molecular weight (C.P.), without laser irradiation (control) and with 1,000 shots with Coomassie Brilliant Blue R250. The band of amylase after 1,000 shots marked by an arrow became thin, and a substance of a molecular weight smaller than 40,000 was found on the anode side by SDS-PAGE.

It seemed that the excimer laser beam cut off the chain molecule C-N, C-C, N-H and C-H in amylase and changed into protein or peptide with a low molecular weight.

The slight difference of UV absorption was observed at the wavelength between 280 nm and 340 nm.

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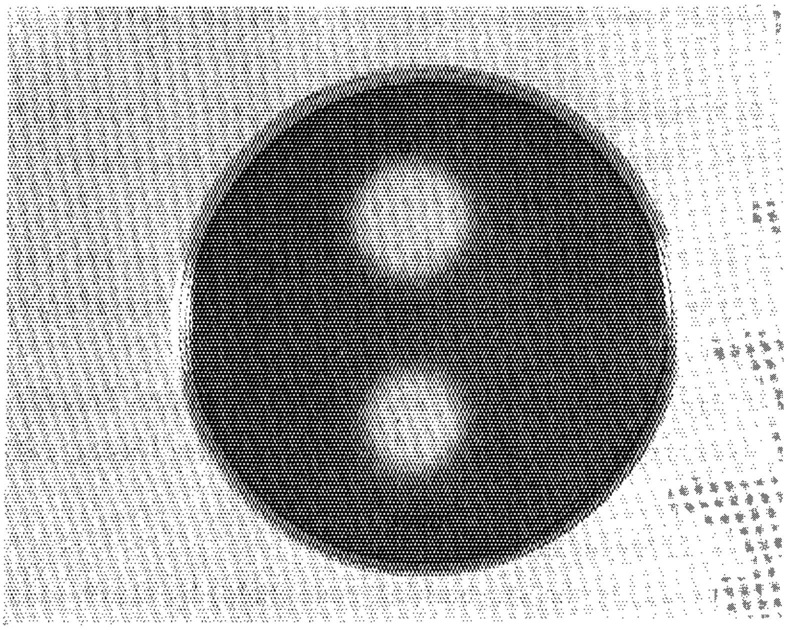

Fig.1 Starch saccharification zone (halo) formed on the starch plate laser-irradiated after incubation for 48hrs. 0:non irradiation, 1000:1000 shots irradiation.

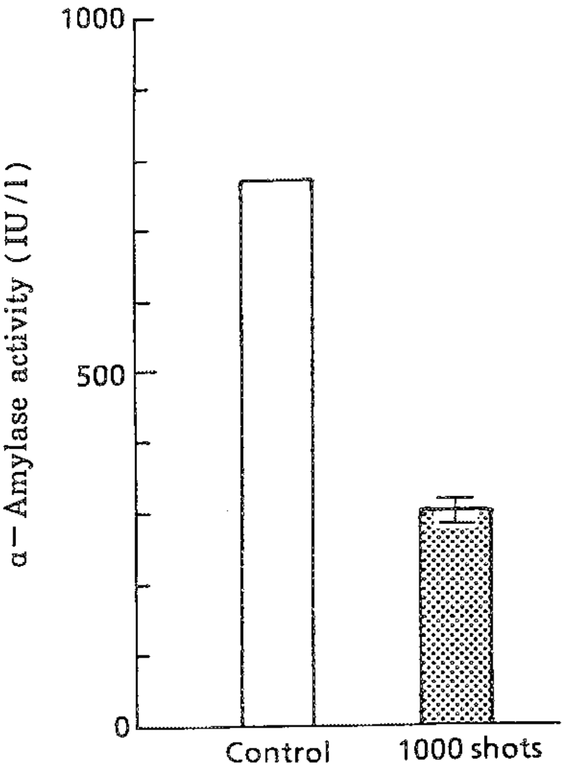

Fig.2 The α-amylase activity after excimer laser irradiation on human salivary amylase.

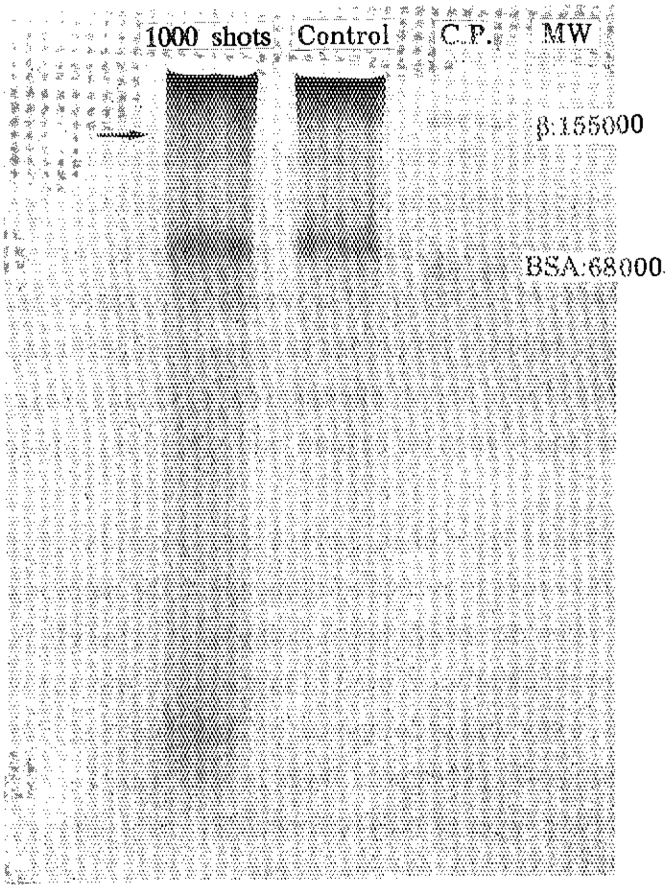

Fig.3 SDS electrophoreses of amylase laser irradiation.
C.P.:Calibration protein (β subunit:RNA polymerase from
E. coli, BSA:albumin from bovine serum),
Control:non irradiation, 1000shots:1000 shots irradiation.

9. Irradiation-effects of Reverse Osmosis Membrane Based on Crosslinked Aromatic Polyamide

Y. Nakase, T. Yanagi,* and T. Uemura**

In reprocessing of spent nuclear fuel, high level radioactive waste (HLW) material is separated from its aqueous solution to reduce its volume. One of a future candidate for this purpose may be separation of the HLW and water by reverse osmosis technique where membrane made of crosslinked aromatic polyamide is to be used.1) This membrane should have superior properties in separation performance with sufficiently high water permeability (flux), and in tolerance for oxidizing reagents and for radiations from radioactive substances such as cesium and strontium nitrates which exist in the HLW solution.

In this paper, studies have been carried out to obtain the data on the radiation effects of membrane materials in wet conditions where the membrane is to be exposed to radiations at the time when the membrane is being used in the HLW solution.

The reverse osmosis membrane used in this study is the one which is manufactured for desalination of sea water and is composed of three layers as shown in Fig. 1; the first layer is crosslinked aromatic polyamide layer of less than 1 μm thickness, the second layer is porous supporting layer of polysulfone (PS), poly (phenylene sulfide sulphone) (PPSS) or oxidized PPSS (PPSO), the total thickness of the layer being 60 μm, and these two layers regarded as one component which is referred as membrane in this report. The third layer is base supporting layer of woven sheet of polyethylene terephthalate of ca. 150 μm thickness, and referred as base material or PET. The reverse osmosis membrane was irradiated as it received, or its component layers, the membrane and the PET, were irradiated and tested separately. The irradiation was carried out using two electron accelerators under 10 cm below the irradiation windows; one, a Van de Graaff accelerator and the other, an accelerator of rectified transformer type. The irradiation conditions were 1.3 MeV, 70 μA and 10 kGy/pass for the former and 0.7 MeV, 1 mA and 100 kGy/pass for the latter.

The irradiated samples (dose: 4 MGy) and unirradiated ones were tested comparatively for their functions. Differential thermal analysis was carried out at heating rate of 20 °C/min for membrane and PET samples. Tensile strength measurements were carried out for dumb-bell shape test pieces of the membrane at an extension rate of 50 mm/min. Separation test (rejection test of solute and flux) on the irradiated reverse osmotic membrane (dose: 0.1-4 MGy) was carried out for 0.15 wt%

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sodium nitrate aqueous solution at 15 kgf/cm^2, 25 °C and pH=6.6 to know the durability of the irradiated membrane.

The heating curves of the irradiated membrane were the same as those obtained for unirradiated membrane. However, as shown in Fig. 2, the heating curve of the PET changed by the irradiation: in the first run of the heating, melting point, Tm, decreased by 20 °C and no glass transition nor crystallization were observed; in the second run of the heating, glass transition, crystallization and melting were observed, and the transition temperatures for the former two did not change, but the melting point decreased by 10 °C by the irradiation.

The relative tensile strengths of the membranes to the corresponding unirradiated ones were plotted as a function of dose in Fig. 3 along with the tensile strength (S_0) of the unirradiated membranes by the corresponding curves. It is noted that the tensile strength of all membranes decreased with dose. Among the three, the membrane of PPSS deteriorated least. After irradiation of 4 MGy, however, the membrane of PS held the highest strength than the other two, even after 60% deterioration by the irradiation, since the original value of the PS membrane (S_0) was the highest (1.33 kgf/cm^2). The results of the separation test of the reverse osmotic membrane were summarized in Table I, where it is shown that rejection of sodium nitrate gradually decreased with increasing dose up to 2 MGy and then decreased to 2.1% at 4 kGy. The original value of flux as defined as the amount of water passed through the reverse osmotic membrane was 1.11 m^3/m^2 d, and the value decreased gradually with increasing dose up to 2 MGy, and then increased to 46.6 at 4 MGy, perhaps due to radiation deterioration of structure of the membrane layer.

Preliminary data were obtained on the effects of irradiation in wet condition on tensile strength, salt rejection and permeability of reverse osmosis membrane used in HLW reprocessing and its components. The results indicate that the reverse osmosis membrane holds practical qualities for HLW experiments up to about 2 MGy and the membrane can be used for separation test of HLW up to 2 MGy.

References

1) M. Kurihara and Y. Himeshima, Polym. J., 23, 513 (1991).

Table 1. Rejection of $NaNO_3$ by reverse osmosis separation with polysulfone(PS) membrane (polyethylene telephthalate(PET) base).

0.15%$NaNO_3$, 15kgf/cm^2, 25℃, pH6.5

Dose MGy	Rejection %	Flux m^3/m^2·d
0	98.9	1.37
0.1	98.0	0.43
0.4	96.5	0.62
1.0	97.4	0.25
4.0	96.5	0.30

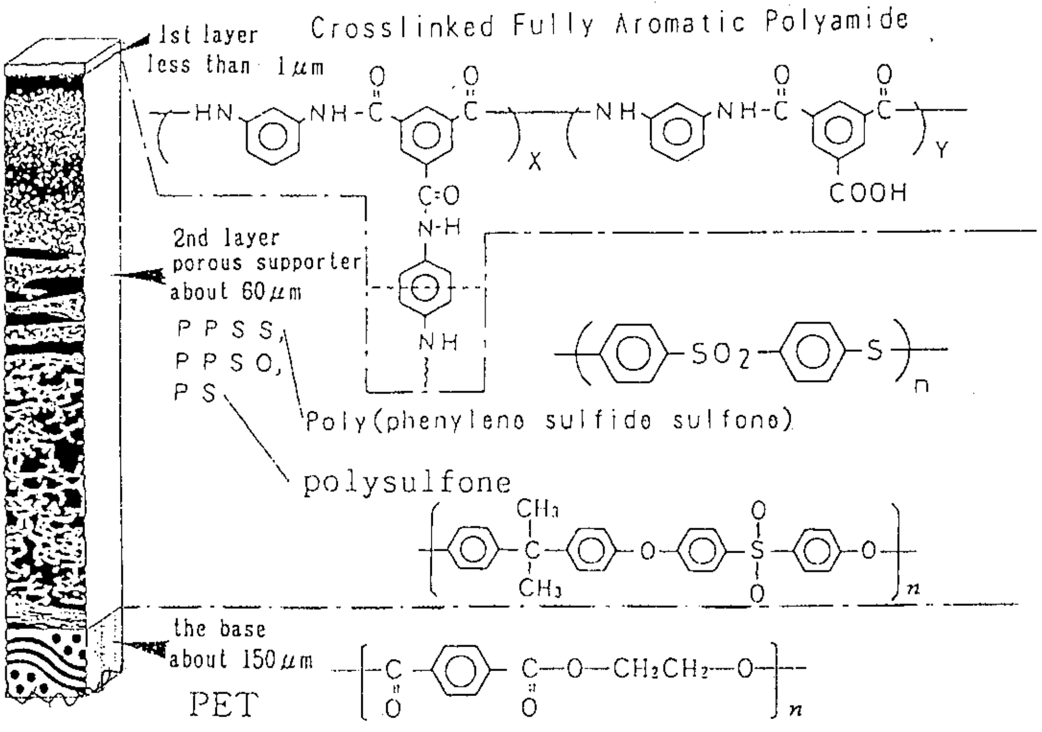

Fig.1. Chemical structures of crosslinked aromatic polyamide as 1st layer, polysulfone, poly(phenylene sulfide sulfone)(PPSS), or oxidized PPSS (PPSO) as 2nd layer, and the construction of reverse osmosis membrane.

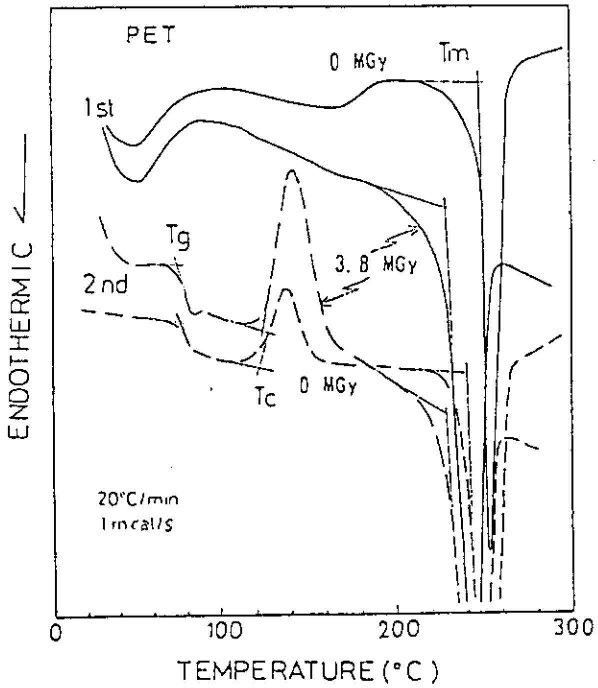

Fig.2. Heating curves of polyethylene telephthalate(PET) as basic material for reverse osmosis membrane irradiated in water and the unirradiated.

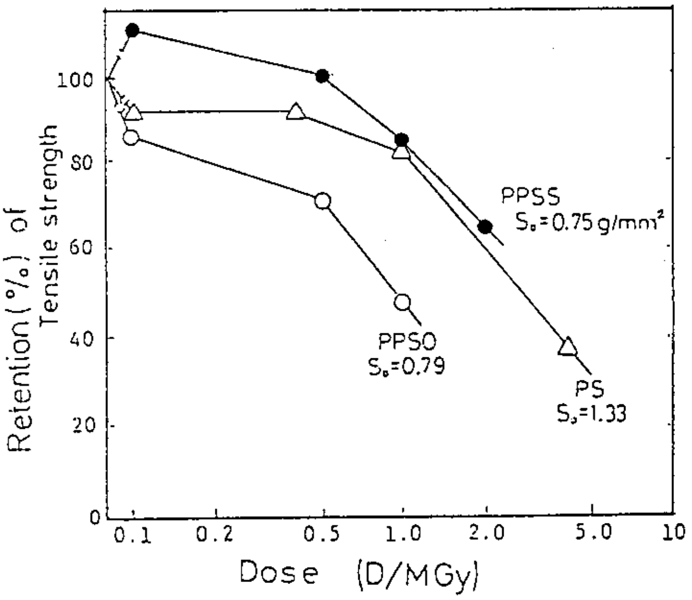

Fig.3. Relationship between retention of tensile strength of membranes, PS, PPSS and PPSO.

10. Radiation-induced Polymerization of Spin Casted Epoxy Films

Y. Nakase, J. Takezaki, M. Hatada, and I. Fujita*

Epoxy resins are chemically stable and exhibit little contraction during the curing process and are therefore recommended as encapsulating and packing materials. Several studies were reported on UV or electron-initiated polymerization of epoxy resin containing initiator in a form of thin casted film of 1 mm thickness1) or spin-casted films of several tens micrometers2). In this paper the polymerization induced by electron beam (EB) or ultraviolet (UV) beam irradiation of thin films of epoxy oligomer resin spin-casted in air has been studied in order to know the rate of polymerization or conversion to polymer in relation to film thickness and depth distribution of energy deposition of the beams.

Epoxy resins used were Epikote 828 and 1001 obtained from Yuka-Shell epoxy Co. Ltd. Bis -4-[-(diphenylsulfonio) phenyl] sulfide-bis hexafluoro phosphate (BDS) was obtained from General Electric Co. Ltd. and used as electron-and photo-initiator. The mixture of 828 and 1001 (1:1 by weight) was dissolved in tetrahydrofuran. Solution of BDS 50 wt% in propylene carbonate was added to the oligomer solution (4:100 by weight) so that the concentration of BDS to oligomer was 2 wt%. The chemical structures of epoxy oligomer and BDS are shown in Fig. 1. The thickness of the spin-casted films was determined from the absorbance at 830 cm^{-1} of phenyl group using molar extinction coefficient of this band previously obtained[2]. Films were irradiated using a Van de Graaff accelerator, a low pressure mercury arc (254 nm), or a high pressure mercury arc (365 nm). The energies deposited in the film of the three beams, EB, UV(254), and UV(365) were estimated on the basis of CTA film dosimetry for EB, and estimated on the bases of molar extinction coefficients of the sample film at 254 and 365 nm and beam intensities at the film surface, and the results are listed in Table 1.

For the polymerization of the oligomer, it was necessary to irradiate the oligomer film with EB or UV (wavelength: above 380 nm) with the presence of BDS. No reaction took place when the oligomer was heated with the presence of BDS at 130 °C for 3 h.

In Fig. 2, conversion of the oligomer to polymer as measured by the decrease of 916 cm is plotted as a function of dose for EB, UV(254), and UV(365), where it is evident that the points obtained for EB come close to those obtained for UV(365) and that the conversions per unit absorbed dose are higher than that obtained for UV(254) where energy deposition of the beam is relatively larger near surface than in the bulk region, whereas the other two gave uniform energy deposition in the film. The results may be explained by that active centers produced uniformly in the film as in the case of

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EB and UV(365) irradiation may extend polymer chain more freely without competing neighboring growing polymer chain.

In Fig. 3, number of monomers reacted per 100 eV absorbed radiation energy (G-value) at initial stage of reaction, at 2 Mrad (3.4 mW•s/cm^2) for EB irradiation and at 5 min (103 mW•s/cm^2) irradiation time for UV(254), is plotted as a function of film thickness. G-value is independent of thickness in the case of EB irradiation, while, it increased with increasing thickness and reached constant value at ca. 10 μm in the case of UV irradiation. The difference between the two cases may be related to the fact that in the EB irradiation, range of electron is extremely long compared to the film thickness, and initiation occurred uniformly in the film independent of the depth. In the UV(254) irradiation, range of UV(254) light is short (half value depth: 2 μm) compared to the film thickness. It is assumed that polymerization did not extend down from the initiation region near surface at early stage of the irradiation, since kinetic chain at early stage of UV(254) irradiation is supposedly short due to possible contamination in the oligomers. This would explain the result that the G-value was almost constant for the film of above certain thickness.

Similar plots are shown in Fig. 4 for data at longer irradiation time and higher dose (60 min: 1.24 W•s/cm^2 and 30 Mrad: 52 mW•s/cm^2, respectively). Contrary to the results at early stage, in the EB irradiation, the G-value increased with increasing thickness and reached constant value above 10 μm thickness, while in the UV(254) irradiation, the value increased linearly with thickness. This may suggest that in the EB irradiation, more islands of unreacted oligomer left at later stage of reaction when the thickness of the film is small, since access of glowing polymer chain to unreacted oligomers is difficult in the extremely thin film. Linear increase of G-value in the UV(254) irradiation may account for that extension of kinetic chain from the near surface region toward bulk phase after consumption of inhibitor becomes easier as the film thickness increased. The fact that G-value is always higher in the EB irradiation than in UV(254) irradiation may be that the decomposition of catalyst to initiate polymerization is limited only at the surface region in UV(254) irradiation while in the EB irradiation, initiation occurred uniformly throughout the film.

The results obtained in the present research are tentatively explained by that migration of the oligomer in the film may be limited as the film thickness becomes thin to comparable degree to the dimension of the oligomer, where migration of the molecules is pseudo-two dimensional, and that active centers formed in densely populated state compete one another resulting decrease of conversion of oligomer to the polymer.

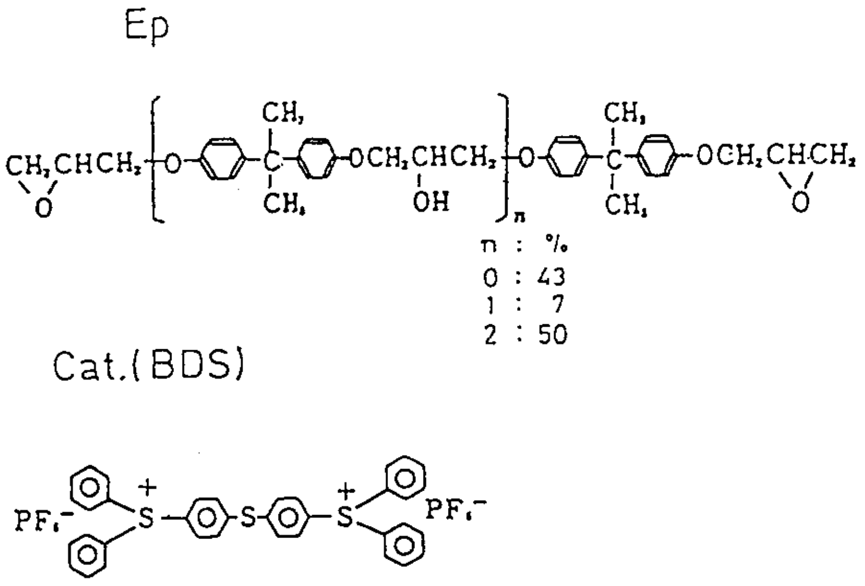
References

1) T. Okada, T. Asano, M. Hatada, J. Takezaki, and K. Ochi, Kobunshi Ronbunshu (Collective papers on polymer science), 44, 761 (1987).

2) I. Fujita, Y. Tanaka, and J. Takezaki, Radiat. Phys. Chem., 40, 161 (1992).

Table 1 Energy deposited in the film

Thickness	beam	surface intensity	transimission	energy absorbed
2.0(μm)	EB	0.1Mrad/s(0.17mW/cm^2)	100.0(%)	2.0Mrad(3.4mW・s)
1.3	UV(254)	0.35 mW/cm^2	33.0	0.23 mW・s
0.7	UV(365)	0.35 mW/cm^2	99.4	0.0014 mW・s



Ep

n : %
0 : 43
1 : 7
2 : 50

Cat.(BDS)

Fig. 1. Chemical formulae of epoxy oligomer and initiator(BDS) and composition of the oligomer of different molecular weight.

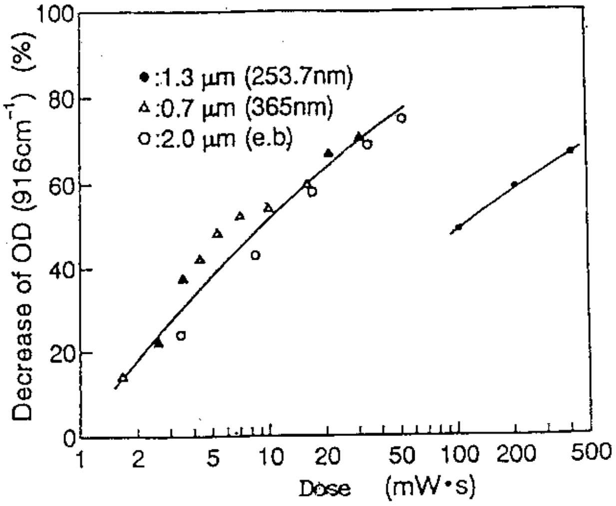


Fig. 2. Conversion of oligomer as a function of dose: ○ EB irradiation, 2.0 μm, ● UV(254) irradiation, 1.3 μm, △ UV(365) irradiation, 0.7 μm.

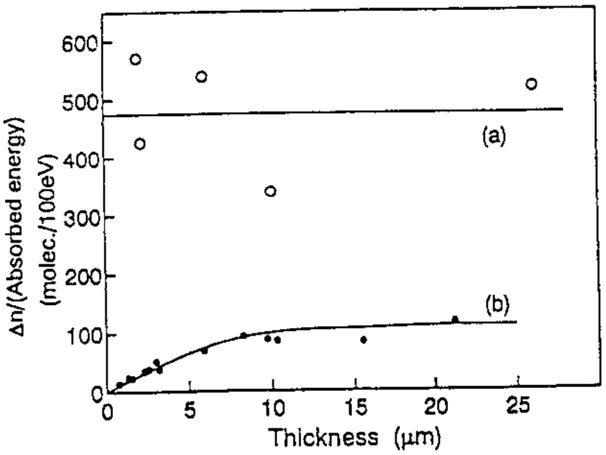


Fig. 3. Number of epoxy groups reacted (△ n) per 100 eV energy absorption at early stage as a function of film thickness; (a) EB (2 Mrad) and (b) UV(254) (3.4 mW・s: 5 min) irradiation.

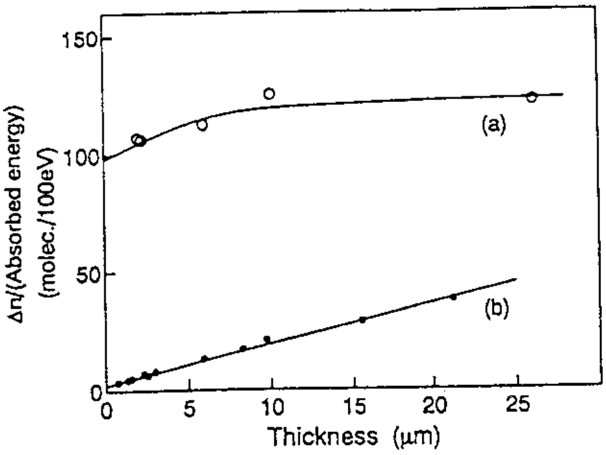


Fig. 4. Number of epoxy groups reacted (△ n) per 100 eV energy absorption at later stage as a function of film thickness; (a) EB (30 Mrad) and (b) UV(254) (1.24 W ・s:60min) irradiation.

11. Formation of a Self-assisted Monomolecular Film Pattern

N. Mino,* K. Ogawa,* and M. Hatada

The purpose of the present study is to know whether a monomolecular pattern can be formed on another monomolecular film which was deposited on a silicone wafer in a hope that the technique to build the monomolecular pattern will be applied to make a molecular electronic device.

Materials used for chemical adsorption film (CA) were 18 nonadecenyl trichlorosilane ($CH_2=CH(CH_2)_{17}SiCl_3$: V-NTS) and 9-(heptadecafluorodecyl-dimethylsilyl) nonyltrichlorosilane ($CF_3(CF_2)7(CH_2)_9SiCl_3$: F17-TS). The monolayer of V-NTS was deposited on a silicon wafer by immersing the wafer in mixed solution (CA solution) of n-hexane and chloroform containing V-NTS. The monolayer on the wafer was irradiated in a stainless steel vessel equipped with an aluminum window at the top, through which electrons penetrated. The atmosphere of the irradiation was nitrogen, the content of oxygen in the nitrogen atmosphere being kept as low as possible below 200 ppm. The irradiation was carried out with electron beam of 300 keV, 100 μA at dose rate of 0.2 kGy/s (as measured by CTA film dosimetry) for 100 s on the monolayer covered with a stainless steel mask (thickness: 1.5 mm, two windows; one, 10×30 mm, and the other, 20×30; each separated with a 2 mm narrow strip). The irradiated monolayer on the wafer was immersed in the CA solution containing F17-TS for CA deposition of F17-TS monolayer on the V-NTS monolayer selectively in the zone which had been exposed to electron beam through the window. The CA deposition of F17-TS was possible because the electron beam irradiation had converted terminal unsaturated group of the V-NTS to NH or NH_2 group which further reacted with trichlorosilane group of F17-TS in the subsequent CA process (Fig. 1a). After the second CA process, the sample was cut out to eight pieces (shown in Fig. 1a) of 8×8 mm which are subjected to XPS measurements to recognize the pattern of F17-TS on V-NTS monolayer.

As shown in Fig. 1b, composition of F is small at sections 1, 2, 7, and 8, where no F17-TS layer would exist, whereas F is detected at sections from 3 through 6. Surface concentration of fluorine atoms on each section is shown in Fig. 1b with the value calculated from fraction of surface area covered with F17-TS on each section. Both observed and calculated agree quite well each other. Surface concentrations of C, Si and O are shown in Fig. 1c. It seems that both siloxane layer and silicon oxide layer in the wafer contribute to observed silicon concentration. The observed decrease of Si concentration in the sections from 3 through 6 may be caused by absorption of escaped photoelectron in the F17-TS layer. The reason that enhancement of O signal was

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* Central Research Laboratories, Matsushita Electric Industrial Company, Ltd.

observed at this region is not known at present, but may be explained by that the contribution of oxygen of the siloxane layer is dominant over that of silicon oxide layer of the wafer.

It is concluded that the F17-TS monolayer was selectively formed on V-NTS monolayer as designed. More elaborate pattern can be made using electron beam drawing. However, development of more sophisticated technique to observe monolayer pattern with higher resolution is indispensable for our future studies.

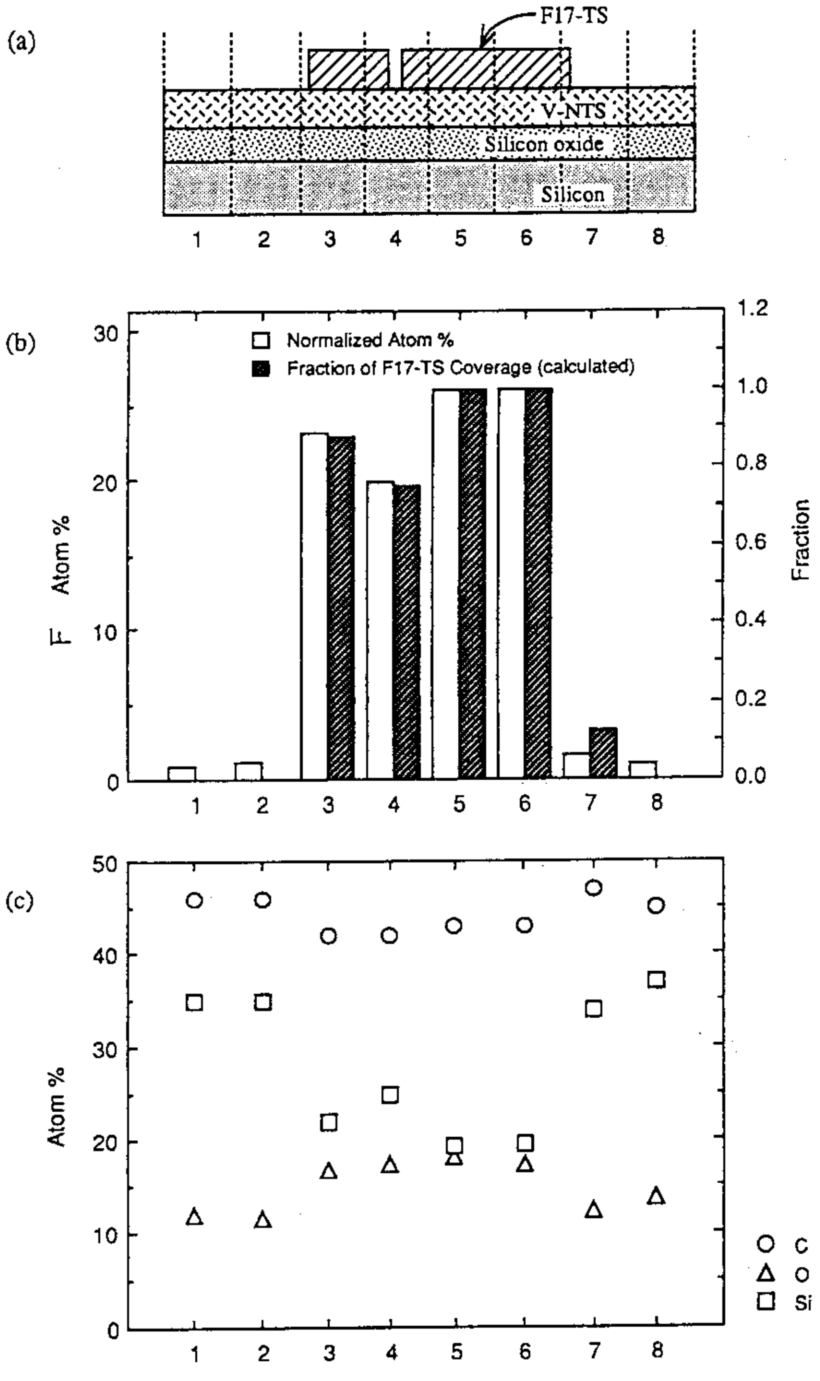

Fig. 1. (a) Schematic drawing of cross section of CA film; (b) Surface concentration of F (normalized); (c) Surface concentration of Si, O, and C.

12. Formation of Solid Particles from Aqueous Solution of Palladium Sulfate and Palladium Sulfate-silver Sulfate by Gamma Ray Irradiation

M. Hatada

Study has been carried out in an attempt to obtain fine metal particles from aqueous solution of metal ions by gamma ray irradiation. The small metal particles of the size between molecules and bulk metal are expected to have some unknown special features which may be interesting for catalysts of high selectivity and activity. The palladium and silver were selected in this study, since these materials attract strong interest in the field of gas-solid heterogeneous catalysis.

Aqueous solution (13 ml) containing 1 mmol/l of palladium sulfate (P) was irradiated with gamma-ray at 10-35 °C in a 18 ml pyrex tubing sealed with a screw cap at the top after the solution was saturated with nitrogen. Dose rate were 2.35 and 11.2 kGy/h and dose was varied from 2 to 120 kGy. After irradiation, the solution was transferred to a cuvette for UV-visible spectrophotometry using a Shimadzu UV3100 spectrophotometer. The amount of unreacted palladium ion was determined from the decrease of the optical density at 398 nm using molar absorption coefficient of 106 mol^{-1}. Similar experiments were carried out on solution containing both palladium sulfate and silver sulfate (PA) and on that containing silver sulfate alone (A).

Figure 1 shows the concentration of palladium ion in the solution as a function of dose for the solutions (P) and (PA) without the presence of oxygen. Change of silver ion concentration with dose is also shown in the figure when the solution (PA) and the solution containing silver ion alone (A) were irradiated without the presence of oxygen. In the solution (P) without oxygen, concentration of palladium ion decreased with increasing dose monotonously and disappeared at 30 kGy. Concentration of silver ion did not decrease with dose when the solution (A) without oxygen was irradiated, but silver ion decreased along with palladium with increasing dose in the solution (PA) without oxygen, and both palladium and silver ions disappeared at about 100 kGy. This result may suggest that particles of palladium-silver alloy are formed by the irradiation. The concentration of palladium ion in the solution is plotted as a function of dose in Fig. 1 for the solution (P) saturated with oxygen. It is evident that oxygen retarded the reduction of palladium ion.

In Fig. 2, turbidity as measured as absorption at 700 nm was plotted as a function of dose for (P) and (PA) without the presence of oxygen at dose rate of 2.35 and 11.2 kGy/h. The turbidity increased sharply with dose and then reached maximum value at 18 kGy when the irradiation was carried out on the solution (P) at 11.3 kGy/h, while turbidity increased gradually, reached maximum at 8 kGy, and decreased with increasing dose when the irradiations were done at 2.35 kGy/h, indicating the presence of the competition of formation of small colloidal particles and growth of the colloidal particles to fine particles which precipitated. Higher turbidity was observed for the solution (PA) than for the solution (A), indicating that the particle size obtained in the former solution is smaller than those obtained from the latter solution. The presence of oxygen was found to retard the formation of small particles which contribute to the turbidity.

Gray palladium particles (9.5 mg) was obtained from 150 ml solution (P) by 142 kGy irradiation which was enough to react all palladium ions in the solution. The yield was calculated to be ca. 60%. Optical microscopic observation was not satisfactory to obtain clear information on particle size or shape of the particles, but only revealed that the particles are aggregate of smaller particles which were smaller than the resolution limit of the microscope.

The study is in progress to obtain information on particle size distribution in relation to reaction conditions such as dose rate, metal ion concentration and composition of metal ions.

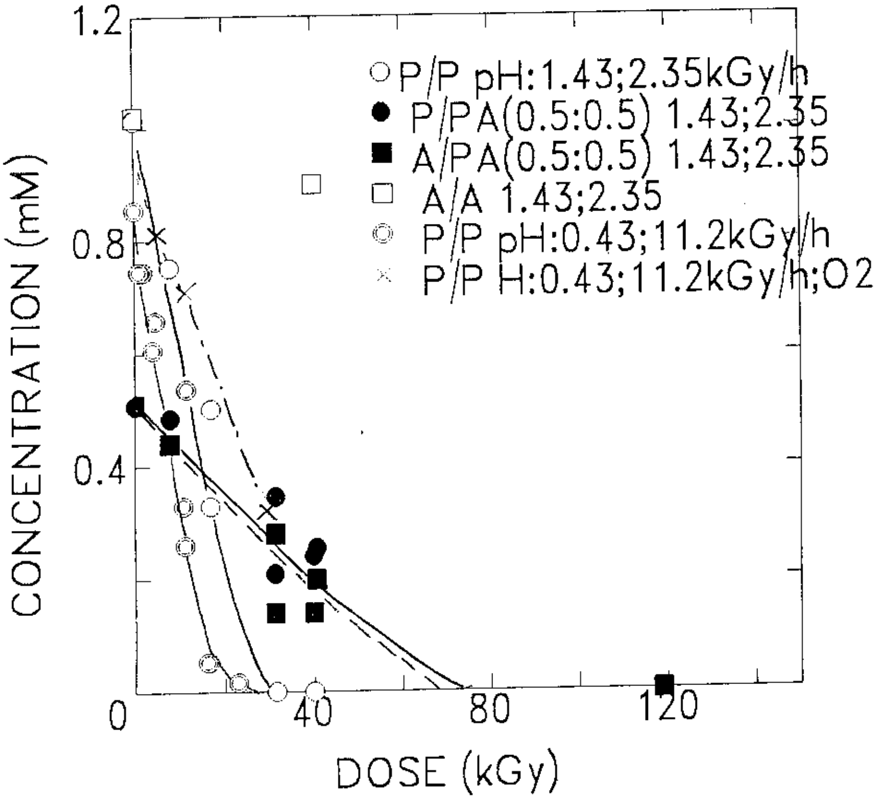

Fig. 1. Concentration of palladium and silver ions in palladium sulfate, palladium sulfate－silver sulfate, and silver sulfate solutions as a function of dose.

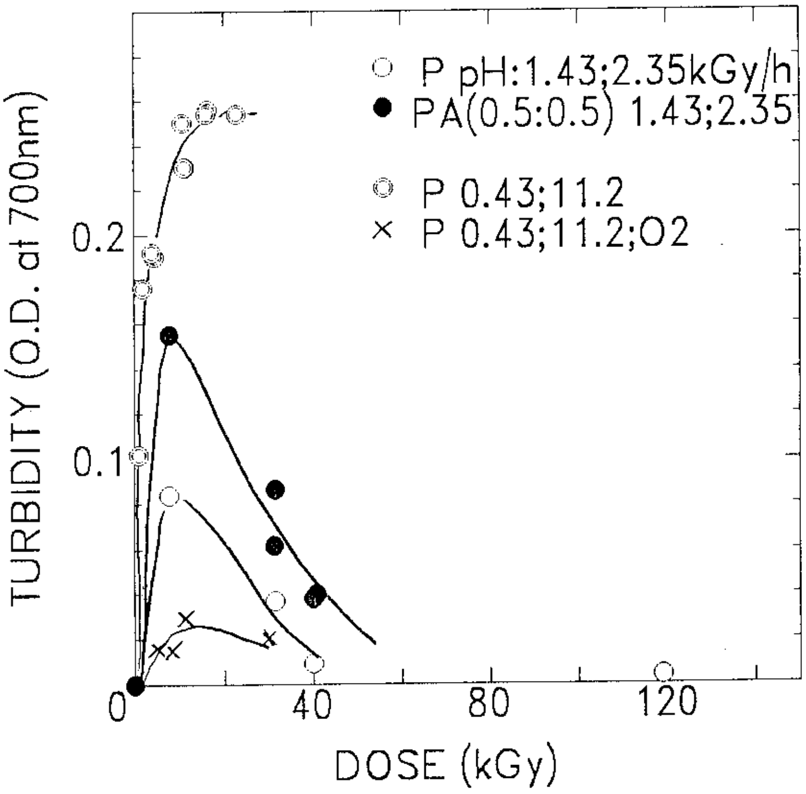

Fig. 2. Turbidity (optical density at 700 nm) as a function of dose.

13. Photo-emission from Excited CO_2 Ion by High Energy Electron Irradiation of Argon-carbon Dioxide Gas Mixture

K. Nakato, K. Yuasa,* I. Fujita,* and T. Kijima

As a series of studies1-4) to obtain data on energy transfer between rare gases and simple molecules, studies on photo emission from gas mixtures of helium and carbon monoxide2) or carbon dioxide4) excited by electron irradiation were carried out. The knowledge of energy transfer from rare gas to the simple molecules would be important for rare gas-sensitized radiolyses of the simple molecules. This year, we have made some measurements on emission spectra from excited states of carbon dioxide (CO_2^{+*}(A,B)) formed by electron irradiation of gas mixture of argon and carbon dioxide in order to study energy transfer scheme involving these species, which explains experimental data of emission intensities obtained under different gas compositions and gas pressures.

Experimental set up and experimental procedures used in the present study are described elsewhere1,2). Carbon dioxide gas and argon gas (both reagent grade) were obtained from Takachiho Chemicals Co. Electron irradiation was carried out with 0.6 MeV electrons from a Van de Graaff accelerator.

Figure 1 shows emission spectra obtained by electron irradiation of carbon dioxide at pressure of 300 Torr. Two emission bands were observed, one due to the $A\Pi$-$X\Pi$ (A-X) transition, and the other $B\Sigma$-$X\Pi$ (B-X) transition from CO_2^{+*}.

In Fig. 2, emission intensities of (B-X) band systems are plotted as a function of partial pressure of carbon dioxide, pressure of argon being taken as a parameter. Table 1 shows a possible reaction scheme tentatively assumed from those established for other mixture of rare gas and simple gases (CO-Ar), (CO_2-He) in the earlier studies2,4). With increasing the partial pressure of carbon dioxide, the emission intensities of (B-X) band increased and then approached to a constant value. This indicates that more CO_2^{+*} were formed by direct excitation of carbon dioxide (reaction (1)) with increasing carbon dioxide pressure, and more quenching of CO_2^{+*} due to collision with carbon dioxide molecules (reaction (2)) occurred when the carbon dioxide pressure increased further. The weak emission is still observed down to low pressure of carbon dioxide below 1 Torr. This may be explained by that CO_2^{+*} is formed by Penning ionization due to collision with excited argon atom (reaction (7)). At the pressures of carbon dioxide of above 1 Torr, the emission intensities decreased with increasing argon pressure, indicating that quenching of CO_2^{+*} due to collision with argon (reaction (4)) took place.

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These results may be explained by the reaction mechanism (Table 1), which further leads to the following equation under a steady state approximation on intermediates:

$$[CO_2^{+*}] = [CO_2] / (k_Q[CO_2] + k_R + k_{QA}[Ar]) \\ \{B_{c2} + k_{c2}B_{Ar}[Ar] / (k_{D2}[Ar] + k_{c2}[CO_2]\} \qquad (1)$$

where B_{c2}, k_Q, k_{c2}, etc. are the rate constants. The species in brackets represent the concentrations of the corresponding species. The first term in equation (1) indicates the amount of CO_2^{+*} formed by direct excitation due to collision with electron, and the steady state concentration of CO_2^{+*} which increases monotonously to a constant value with increasing carbon dioxide concentration. The second term indicates the amounts of CO_2^{+*} formed by Penning ionization due to collision with excited argon atoms, and the steady state concentration of CO_2^{+*} becomes a maximum at carbon dioxide concentration given by equation (2):

$$[CO_2] = \{k_R k_{D2}[Ar] / (k_Q k_{c2})\}^{1/2} \qquad (2)$$

For infinitely large carbon dioxide concentration in equation (1), concentration of carbon dioxide becomes constant value as given by equation (3):

$$\lim_{[CO_2] \to \infty} [CO_2^{+*}] = B_{c2} / k_Q \qquad (3)$$

This agrees well with the experimental result that the emission intensities from excited species approach a constant value with increasing carbon dioxide pressure. The second term of equation (1) may account for the small increase observed for emission intensities at low pressure of carbon dioxide.

Results obtained observed for emission band systems (A-X) were too complex to allow kinetic analysis. Perhaps additional reactions in the scheme may be necessary to explain the observed data.

Intensities of photo-emission for argon-carbon dioxide mixture are not much different from those observed for helium-carbon dioxide mixture, regardless of higher density of argon than that of helium. The emission spectra observed for argon-carbon dioxide mixture is also similar to that obtained for helium-carbon dioxide mixture. Further detailed comparative study on the rate data for the two mixtures will be carried out.

References

1) K. Matsuda, et al., Appl. Radiat. Isot., 41, 757 (1990).
2) K. Matsuda, et al., Appl. Radiat. Isot., 42, 1223 (1991).
3) I. Fujita, et al., Appl. Radiat. Isot., 43, 641 (1992).
4) K. Nakato, et al., unpublished data.

Table 1 Reaction scheme

Reactant		Product	Rate Constant	Type of reaction
$CO_2 + e$	$\longrightarrow$	CO_2^{+*}	B_{c2}	Excitation
$CO_2^{+*} + CO_2$	$\longrightarrow$	$CO_2^{+} + CO_2$	k_Q	Quenchig
CO_2^{+*}	$\longrightarrow$	$CO_2^{+} + h\nu$	k_R	Radiation
$CO_2^{+*} + Ar$	$\longrightarrow$	$CO_2^{+} + Ar$	k_{QA}	Quenchig
$Ar + e$	$\longrightarrow$	Ar^{*}	B_{Ar}	Excitation
$Ar^{*} + Ar$	$\longrightarrow$	$Ar + Ar$	k_{D2}	Deactivation
$Ar^{*} + CO_2$	$\longrightarrow$	$Ar + CO_2^{+*}$	k_{C2}	Excitation Transfer

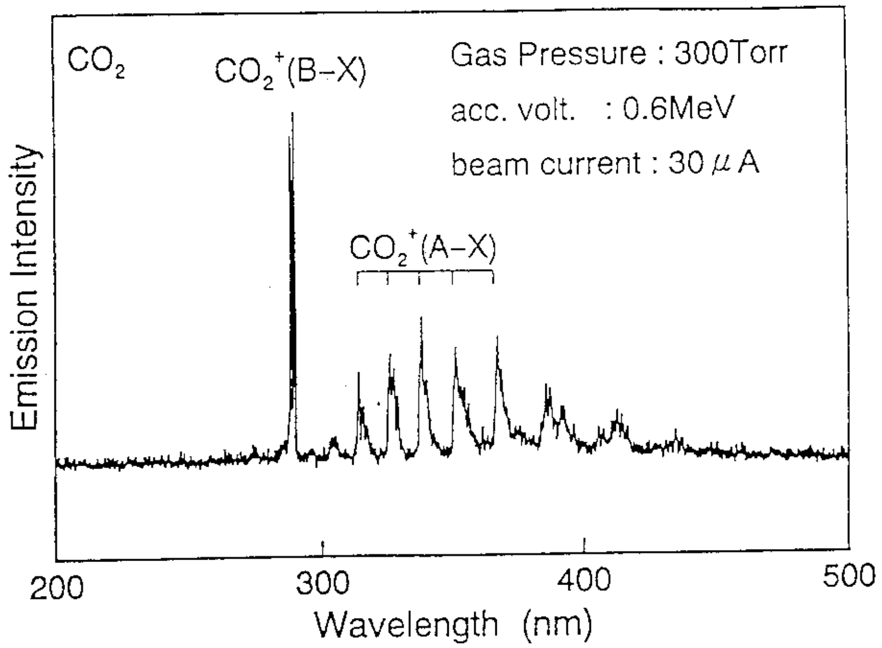

Fig. 1 Emission spectra of carbon dioxide at pressure of 300 Torr

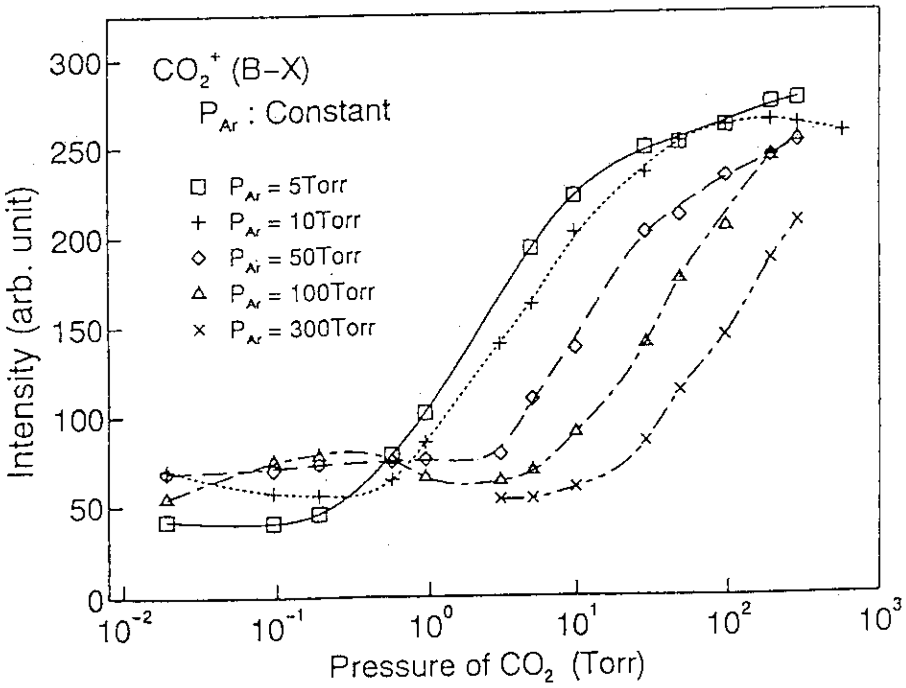

Fig. 2 Emission intensities of (B-X) band

14. Electron Beam Dosimetry for a Thin-layer Absorber Irradiated by Low-energy Electrons

T. Kijima, K. Nakato, and Y. Nakase

Irradiation by low-energy electrons below 1 MeV is widely used for curing of thin-layer coatings, laminates of smaller than several tenth millimeter thickness. In order to measure the dose absorbed by such a thin layer substance, we obtained depth-dose distribution curves for 300 keV electrons of spot beam which hits the sample surface perpendicularly using a thin CTA film dosimeter of 38 μm thickness[1]. However, in the practical radiation processes, electron accelerators of scanning horn type are mainly used, where the beam is scanned in the direction perpendicular to the travelling of the sample on a conveyor. In this circumstance, the sample carried on a conveyer receives oblique electron beam before the sample enters into the radiation field under the irradiation window, and the thin sample layer is often supported on backing material of high atomic numbers. Therefore, for accurate dosimetry of these samples, it is further necessary to obtain depth-dose distribution when the electron beam impinges into the sample surface with different angles and when the sample is placed on material of relatively high atomic number from which electrons are scattered back into the sample.

We have measured the dissipation of energy of an electron in calibrated CTA film dosimeter stack, where 300 keV electrons penetrated through a Ti irradiation window foil (30 μm) and air (10 cm) in the same way as in the previous paper[1]. The CTA film stack was a build-up of the 38 μm thick CTA films (1.30 g/cm^3, width 8 mm) with total thickness of 5 mm or larger. The calibrated sensitivity to radiation (k value) of the CTA film was 1.9 ΔOD/MGy. The film stack was placed on a conveyer and irradiated under moving condition (dynamic) or irradiated under static condition under the irradiation window. In the experiments to obtain depth-dose distribution for oblique incidence of the beam, the CTA film stack was placed under the irradiation at different angles to the direction of electron beam. The effect of backscattering was studied using tin plate (Sn) as a backing material. After the irradiation, the CTA films in the stack were subjected to optical density measurement separately at 280 nm to obtain depth-dose distribution.

An accelerator of a rectified transformer-type with a scanning hone was used for irradiation in the present study. Beam current was 0.2 mA and velocity of the conveyer was 8 mm/s. A scanning width of the electron was set at 15 cm at the irradiation window.

Figure 1 shows the depth-dose distribution in the stack as a function of thickness for the two irradiation conditions, one dynamic and the other, static one comparatively.

The depth-dose distribution curve for the dynamic irradiation shows the peak closer to the surface than that for the case of the static irradiation.

In Fig. 2, the depth-dose distribution curves are shown for different incident angles of electron beam to the normal of the sample (at 0 degree, electrons hit the surface perpendicularly). As the incident angle increased, energy dissipation in near surface layers (first 2 or 3 layers) increased, while that in the deeper layers, below the 6th layer, decreased. The result can be understood when one takes into account the increasing effective depth with increasing incident angle.

Figure 3 shows a cross section of the CTA stack on a tin substrate perpendicular to the direction of beam scanning with a set of contour lines of equi-dose in the CTA stack. The doses are normalized to the dose of the surface at 0 degree incidence without any backing material. About 25% increase of the dose was observed at the center of the beam due to the electrons back-scattered from the substrate.

Above results indicate that for accurate dosimetry of thin material of several tenth millimeters when the material is irradiated with low energy electrons (ca. 300 keV) on a conveyer travelling under irradiation window of an accelerator of scanning type, it is necessary to consider the effects of backscattering from substrate, and of oblique incidence of electrons.

Reference

1) K. Matsuda et al., JAERI-M 90-054, 48 (1990).

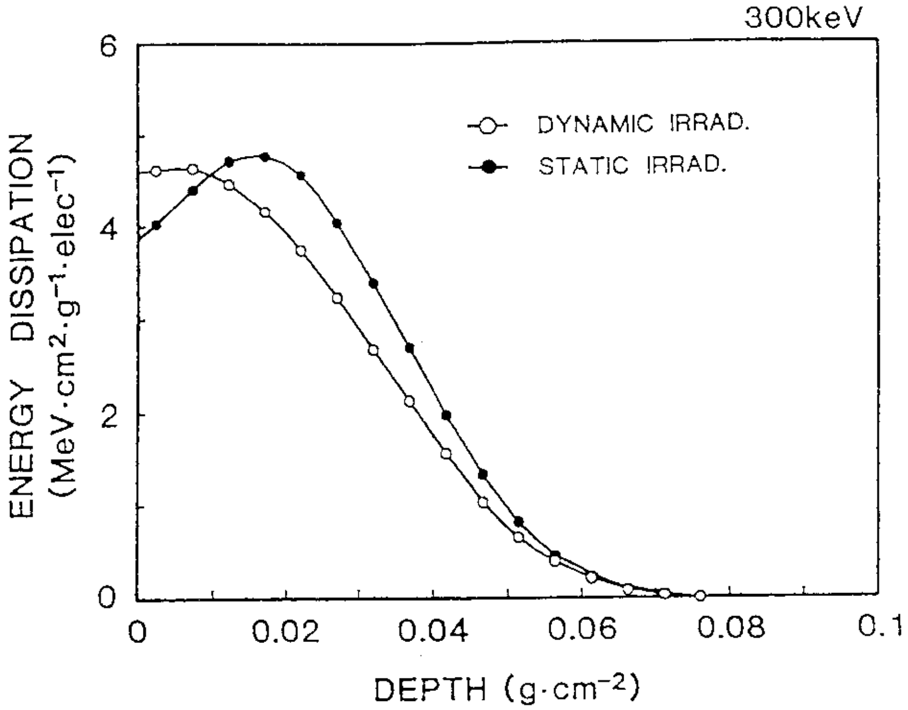

Fig. 1. Energy dissipation(depth-dose) distributions for 300-keV electrons in totally absorbing CTA film stacks with dynamic and static irradiation.

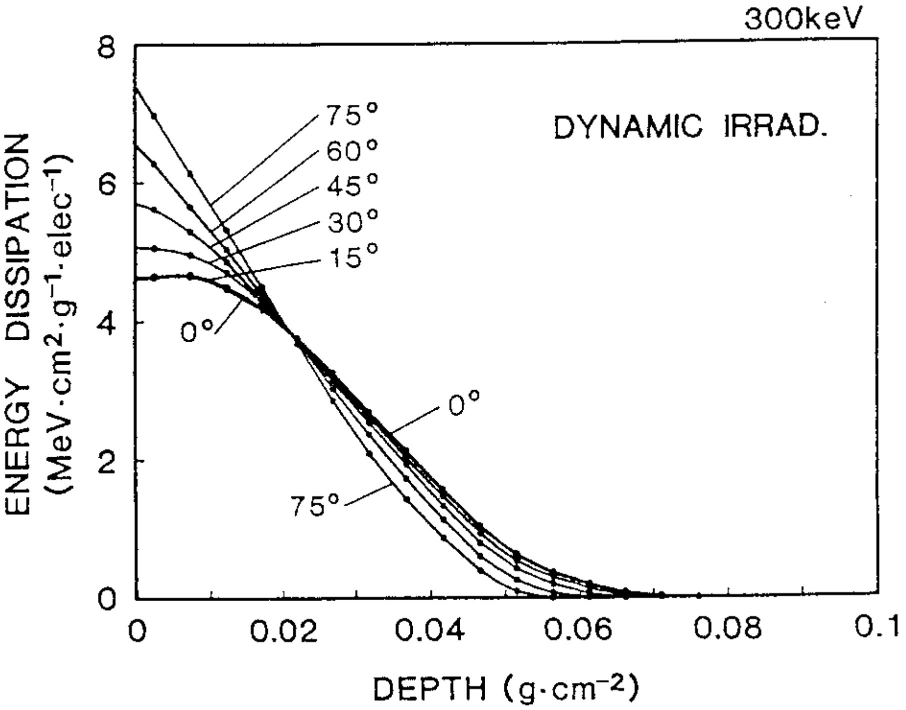

Fig. 2. Depth-dose distributions for 300-keV electrons in totally absobing CTA film stacks inclined to the beam direction, in the case of dynamic irradiation.

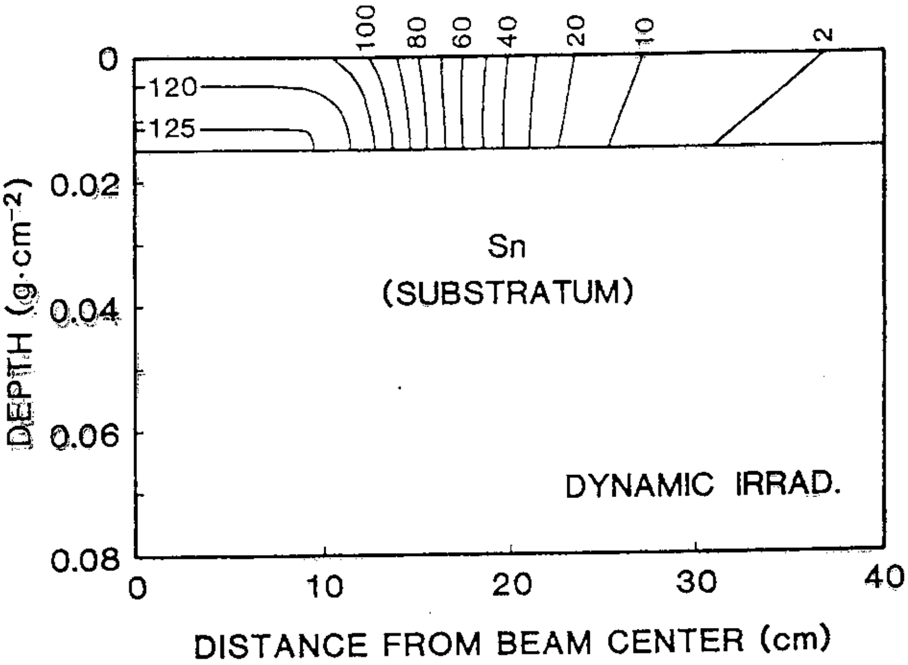

Fig. 3. The contour map of dose distribution (different dose in kGy) in the thin layer of CTA on the Sn substrate along the scanning direction, in the case of dynamic irradiation.

15. Operation and Maintenance of Irradiation Facilities

K. Nakato

The irradiation facilities in our laboratory were operated for research performed in the laboratory and cooperative studies with universities and industries, as well. However, some repairing services were necessary for the accelerators.

The Van de Graaff accelerator (No. 1 accelerator) was operated satisfactory, until mid May, when the vacuum pumping of the machine had to be interrupted for a few days due to maintenance job to an electric power supply system of the laboratory. After the power system was recovered, the vacuum pumping of the machine was restarted, but the vacuum in the accelerator tube failed to go over 10^{-3} Torr regardless of extensive pumping for a few days. Cleaning and reassembling of the vacuum parts which took two weeks returned the machine to the normal condition. Later, automatic safety valves were added to the vacuum system so that they keep the accelerator tube in vacuum condition in case of unexpected power failure.

The accelerator of a transformer type (No. 2 accelerator) was operated satisfactory in the first quarter without any serious trouble, but it suddenly went out of service on July 28th due to insulation failure of a solid cable which feeds high voltage from the transformer to the electron gun in the accelerator tube. The accelerator is hung from a ceiling crane and one can move the accelerator just above a complex experimental assembly for irradiation. The cable is called "solid" cable but it is flexible enough to allow the accelerator to move. The insulation of the solid cable seems to be deteriorated by repeated stretch and bend movements of the cable accompanied by the movement of the accelerator. The present solid cable was installed in 1980 in place of the first one which had originally been installed in 1975 when the accelerator was initially operated.

Since the solid cables are no more available at present, the cable was replaced with an OF (oil filled) cable sacrificing convenience of the movable operation of the accelerator. Therefore the accelerator had to be fixed at the center of the room and the irradiation window of the accelerator is 1.5 m above the floor level. Further, a maintenance hatch was built in the upper part of the tank for easy access to an electron gun assembly for maintenance job without removing the OF cable.

The modification and repair of the accelerator were completed at the end of March 1993, and the accelerator was ready for service. One advantage of the modification is that the time required for charging up the gun is reduced significantly, and this allows the users to save time. The charging time required for 800 kV reduced to 10 min from 30 min as it was before the repair job.

The cobalt-60 irradiation facility was operated satisfactory throughout the fiscal 1992.

Operation of the facilities was also made for irradiation service to industrial companies. The annual operation of the facilities is given in Table 1.

Table 1 Utilization and operation of the facilities during fiscal 1992

	Van de Graaff accelerator (No. 1)	Accelerator of Transformer type (No. 2)	Cobalt 60 gamma ray source
Beam generation time	(hour:min) 151:59	(hour:min) 18:32	(hour:min) 5004:09
Number of experiments			
JAERI	76	14	77
Universities	0	0	0
Industries	30	8	15
Research Organizations	0	0	0
Total	106	22	92

III. List of Publications

1. Published Papers

Y. Shimizu, "Excimer Laser-Induced Organic Transformation of Alcohol", Report of Laser Technology, No.69, 50 (1992).

M. Hattori, Y. Ishikawa, K. Mizuno, S. Arai, S. Sugimoto, Y. Shimizu, S. Kawanishi, and N. Suzuki, "13C-Selective IRMPD.of CBrClF2", Appl. Phys. B, 55, 413 (1992).

S. Kawanishi, S. Sugimoto, Y. Shimizu, and N. Suzuki, "Laser Irradiation Effects on Polyetheretherketone studied by X-ray Photoelectron Spectroscopy", Proc. Int. Conf. on Evo. Beam Appl. (Takasaki) p.666-9 (1991).

Y. Shimizu, S. Kawanishi, S. Sugimoto, and N. Suzuki, "Laser-Induced Selective Synthesis of Diols from Methanol and Ethanol in the Presence of Hydrogen Peroxide", Proc. Int. Conf. on Evo. Beam Appl. (Takasaki) p.670-5 (1991).

S. Kawanishi, S. Sugimoto, Y. Shimizu, and N. Suzuki, "Excimer Laser Irradiation Effects on Fluoropolymers and Aromatic Polymer", J. Photopolym. Sci. & Tech., 5, 271 (1992).

Y. Shimizu, S. Sugimoto, M. Nishii, and N. Suzuki, "Direct Synthesis of Hydroxy Acid from Maleate Aqueous Solutions Containing Hydrogen Peroxide Using an Excimer Laser", Chem. Express, 7, 633 (1992).

M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, M. Nagase, M. Endo, and Y. Eguchi, "Surface Modification of Polytetrafluoroehylene by KrF-Laser Irradiation", Chem. Lett. 1992, 2089.

M. Nishii, "Modification of Adhesive Properties of Fluorine Resins by Laser Light" (Japanese), Nuclear Engineering, 39, 56 (1993).

J. Takezaki, Y. Tanaka, and I. Fujita, "Polymerization of Spin-Casted Epoxy Films Induced by Electron Beam or UV Irradiation", Radiat. Phys. Chem., 40, 161 (1992).

N. Mino, K. Ogawa, and M. Hatada, "Control of Reactivity to Energy Beams on Chemically Adsorbed Monolayer from Polydicacetylene Derivatives", Thin Solid Films, 210/211, 790 (1992).

Y. Nakase, J. Takezaki, and M. Hatada, "Study on Formation of Fine Solid Particles Induced by Radiation", KURRI-TR-368, 33 (1992).

Y. Nakase, "Industrial Applications of Electron Beam", Color Materials, 66, 19 (1992).

Y. Yokota, H. Kotsuka, J.S. Ma, A. Hiraki, H. Kawarada, K. Matsuda, M. Hatada, "Formation of optical centers in CVD diamond by electron and neutron irradiation", Diamond Relat. Mater., 1, 470 (1993).

T. Kijima and Y. Nakase, "Electron Beam Dosimetry for a Thin-Layer Absorber Irradiated by 300-keV Electrons", Appl. Radiat. Isot., 44, 693 (1993).

K. Kaji, Y. Abe, M. Murai, N. Nishioka, and K. Kosai, "Radiation-Grafting of Acrylic Acid onto Ultrahigh Molecular, High-Strength Polyethylene Fibers", J. Appl. Polym. Sci., 47, 1427 (1993).

2. Oral Presentations

S. Kawanishi, S. Sugimoto, Y. Shimizu, and N. Suzuki, "Excimer Laser Irradiation Effects on Fluoropolymer and Aromatic Polymer", The 9th Photopolymer Conference (Tokyo), June 25, 1992.

Y. Shimizu, S. Sugimoto, S. Kawanishi, and N. Suzuki, "Laser-Induced Direct Selective Synthesis of Diols from Alcohols Containing Hydrogen Peroxide", The 14th IUPAC Symp. on Photochemistry (Leuven), July (1992).

M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, T. Nagase, M. Endo, and Y. Eguchi, "Surface Modification of Polytetrafluoroethylene by Excimer-Laser Irradiation (3) Improvement of Adhesive Properties with Blending of PEEK and PI", The 64th Annual Meeting (Autumn) of the Chemical Society of Japan (Niigata), Oct. 1992.

T. Nagase, M. Endo, Y. Eguchi, M. Nishii, S. Sugimoto, Y. Shimizu, and N. Suzuki, "Surface Modification of Polytetrafluoroethylene by Excimer-Laser Irradiation (4) Improvement of Adhesive Properties with Blending of Inorganic Compounds", The 64th Annual Meeting (Autumn) of the Chemical Society of Japan (Niigata), Oct. 1992.

K. Onishi, S. Arai, S. Sugimoto, Y. Shimizu, and N. Suzuki, "Irradiation Effects of Excimer Laser on Polyphenilenesulphide", The 64th Annual Meeting (Autumn) of the Chemical Society of Japan (Niigata), Oct. 1992.

Y. Shimizu, S. Sugimoto, M. Nishii, and N. Suzuki, "Laser-Induced Photochemical Reactions of Maleic Acid Aqueous Solutions in the Presence of Hydrogen Peroxide (2) Effects of Maleate on the Formation of Oxy Acid", The 64th Annual Meeting (Autumn) of the Chemical Society of Japan (Niigata), Oct. 1992.

M. Nishii, S. Sugimoto, Y. Shimizu, S. Sugimoto, N. Suzuki, S. Kawanishi, T. Nagase, M. Endo, and Y. Eguchi, "Improvement of Adhesive Properties of Polytetrafluoroethylene by Excimer-Laser Irradiation. Roles of Changes in Chemical State and Morphology", The 13th Symposium on the Laser Society of Japan (Toyonaka), Jan. 1993.

T. Nagase, M. Endo, M. Nishi, S. Sugimoto, Y. Shimizu, and S. Kawanishi, "Surface Modification of Polytetrafluoroethylene with Plasma treatment by Excimer-Laser Irradiation", The 65th Annual Meeting (Spring) of the Chemical Society of Japan (Tokyo).

M. Nishii, S. Sugimoto, Y. Shimizu, N. Suzuki, S. Kawanishi, T. Nagase, M. Endo, and Y. Eguchi, "Surface Modification of Polytetrafluoroethylene by Excimer-Laser Radiation", The 205th American Chemical Society National Meeting (Denver), March 1993.

T. Kijima, Y. Nakase, "Measurement of dose of 300 keV electrons from a scanning type electron beam irradiation facility", Annual Meeting of the Society of Electronic Communication and Information Process, Oct. 30, 1992, Tokyo.

3. Patent Applications

M. Nishii, N. Suzuki, S. Sugimoto, Y. Hirajima, M. Endo, and T. Nagase, "A Method of Surface Modifying of Polytetrafluoroethylene by Ultraviolet-Laser Light", Japan Patent Appl., 4-145, 595 (1992).

M. Nishii, Y. Shimizu, S. Kawanishi, S. Sugimoto, T. Tanaka, and Y. Eguchi, "A Method of Surface Modifying of Fluorine Resins by Ultraviolet-Laser Light", Japan Patent Appl., 4-327, 822 (1992).

A. Okada, Y. Shimizu, S. Kawanishi, M. Nishii, and S. Sugimoto, "Wettable Fluorine resin", Japan Patent Appl., 5-026, 367 (1993).

IV. List of Cooperative Studies

Effect of laser beam irradiation on polymer materials: Faculty of engineering, Osaka University

Chemical reactions of organometallic compounds induced by laser beam irradiation: Material Science and Technology, Kyoto Institute of Technology

Polymerization of thin layer of epoxy oligomers: Faculty of engineering, Oita University

Strength of irradiated PVA thin films: Institute of bio-medical engineering, Kyoto University

Light emission from gases under electron irradiation: Osaka Electro-communication University

Lattice diffects of silicon and germanium as studied by photo-luminescence method: Naruto College of Education

Effects of laser beam irradiation on bio-related materials: Department of Preventive Dentistry, Ohu University

Distribution of trapped electrons in plastic thin layer: Osaka Institute of Technology

Radiation damage produced in diamond thin layer produced by electron beam irradiation: Faculty of engineering, Osaka University

Fine fabrication of functional membrane for separator: Faculty of engineering, Osaka University

Formation of ultra-fine pattern in self-assembled multi-layers: Matsushita Electric Industries, Co.

Surface modification of fluorine containing polymers by laser beam irradiation: Kurabo Industries, Ltd.

V. List of Personnel

Dr. Masafumi Nakano, director

Prof. Seizo Okamura, invited researcher
Dr. Motoyoshi Hatada, special principal scientist

OFFICE OF ADMINISTRATION
Mr. Yoshiaki Kanda, administrative manager
Mr. Yasushi Tamura
Mrs. Atsuko Hayashi
Mrs. Harumi Ogata [8]

STUDY ON LASER-INDUCED ORGANIC CHEMICAL REACTIONS
Dr. Shunichi Kawanishi, leader
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Dr. Masanobu Nishii
Mr. Shun'ichi Sugimoto [1]
Mr. Tomohiro Nagase [3]
Mr. Tadaharu Tanaka [3]
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Mr. Yuji Hamada [4]
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STUDY ON BASIC RADIATION TECHNOLOGY FOR FUNCTIONAL MATERIALS
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Dr. Norihisa Mino [3]
Dr. Kazufumi Ogawa [3]
Mr. Katsuyuki Yuasa [6]
Mr. Tohru Naitoh [6]

OPERATION AND MAINTENANCE OF IRRADIATION FACILITIES

Mr. Kiyori Nakato, general manager
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Previous reports in this series are:
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Fundamental Studies in the Osaka Laboratory for Radiation Chemistry (Annual Report) No. 1, JAERI 5018 (1967); No. 2, JAERI 5022 (1968); No. 3, JAERI 5026 (1969); No. 4, JAERI 5027 (1970), No. 5, JAERI 5028 (1971); No. 6, JAERI 5029 (1972); No. 7, JAERI 5029; No. 7, JAERI 5030 (1973).
Annual Report of the Osaka Laboratory for Radiation Chemistry, No. 8, JAERI-M 6260 (1974); No. 9, JAERI-M 6702 (1975); No. 10, JAERI-M 7355 (1976); No. 11, JAERI-M 7949 (1977); No. 12, JAERI-M 8569 (1978); No. 13, JAERI-M 9214 (1979); No. 14, JAERI-M 9856 (1980); No. 15, JAERI-M 82-192 (1981); No. 16, JAERI-M 83-199 (1982); No. 17, JAERI-M 84-239 (1983); No. 18, JAERI-M 86-051 (1984); No. 19, JAERI-M 87-046 (1985); No. 20, JAERI-M 88-272 (1986); No. 21, JAERI-M 90-054 (1987); No. 22, JAERI-M 91-054 (1988); Nos. 23, 24, 25, JAERI-M 92-129 (1992).