Proton irradiation effects on several organic polymers

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High-energy (8 MeV) proton irradiation effects on the mechanical properties of polymers (about 100 μm thickness) with various constituents and chemical structures were studied by tensile tests and compared with those caused by 2 MeV electrons. In the aliphatic polymers studied (PE, PP, EVA, PVDF, ETFE and nylon 6), there is scarcely any difference in the absorbed dose dependence of the tensile strength and ultimate elongation between proton and electron irradiation. In the aromatic polymers studied (PET, PES, U-PS and U-polymer), however, the decrements in the tensile strength and ultimate elongation against proton dose are less than that in electron irradiation. In this manner, linear energy transfer effects were scarcely observed in the aliphatic polymers but were clearly observed in the aromatic polymers.

(Keywords: proton; electron; aliphatic polymers; aromatic polymers; mechanical properties)

INTRODUCTION

Ion-beam-induced modifications of chemical and physical properties on the surface of polymer materials have been extensively studied[1–8]. Hioki *et al.*[1] reported that the specific resistivity of Kapton H film irradiated by 0.3–1 MeV N_2^+ ions was surprisingly decreased and that this modification resulted from the decomposition and subsequent carbonization of polymer induced by ions that stop near the surface.

On the other hand, ion irradiation effects under conditions in which ions pass entirely through polymer materials have not been studied so much, in spite of being an important subject in applications of organic materials in radiation fields such as space. The most interesting subject in such studies would be the effect of spatial energy deposition rate per track of ions in materials (dE/dx, linear energy transfer (LET)).

Foti *et al.*[9–12] studied ion irradiation effects on the molecular-weight distribution of monodisperse polystyrene and reported that LET effects were not observed in irradiation by 100 keV He^+, 200 keV Ne^+ and 400 keV Ar^+. In contrast, Aoki *et al.*[13] reported the existence of an LET effect in the *G*-value of crosslinking of polystyrene under irradiation of 0.4–3.3 MeV protons and 0.4–3.0 MeV He^+. There are some reports on LET effects on changes in chemical structure[14–19] and in mechanical properties[20–22], but uncertainty exists.

The tensile strength and elongation of polypropylene usually decrease with dose of electrons and/or γ-rays, while Guang-hou *et al.*[20,21] reported that those increase with dose in irradiation by 20 and 100 keV protons. This result would not express characteristics of proton irradiation effects, because the range ($\sim 4\,\mu$m) of 100 keV protons is too small compared with the thickness of specimens (50 μm). Coulter *et al.*[22] reported that *G*-values (number of reacted molecules per 100 eV) of crosslinking and chain scission of poly(aryl sulphone) irradiated by 3 MeV protons are the same as the reported values obtained by γ-ray irradiation, but there are differences in mechanical damping between proton and electron irradiation.

Thus, characteristics of proton irradiation effects on mechanical properties of organic polymers have not been clarified. The main reason for such few data would be the lack of techniques to irradiate uniformly an area wide enough to measure the mechanical properties. This study was planned to obtain generalized knowledge of high-energy proton irradiation effects on mechanical properties. A chamber was specially constructed to allow a wide area of polymer films to be irradiated uniformly. Then the proton irradiation effects on mechanical properties for wide varieties of polymers having various constituents and chemical structures were studied by measuring tensile properties and compared with the electron irradiation effects.

EXPERIMENTAL

Samples

The samples used were six kinds of aliphatic and four kinds of aromatic polymers. The aliphatic polymers were: polyethylene (PE), isotactic polypropylene (PP), ethylene–vinyl acetate copolymer (EVA), poly(vinylidene fluoride) (PVDF), tetrafluoroethylene–ethylene copolymer (ETFE) and nylon-6. The aromatic polymers were: poly(ethylene terephthalate) (PET), poly(aryl ether sulphone) (PES), bisphenol A based poly(aryl sulphone) (Udel polysulphone, U-PS) and poly(aryl ester)(U-polymer). These samples were received in a film of about

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100 μm thickness. Their chemical structures are shown in *Figure 1*.

Irradiation

Irradiation was performed using 8 MeV protons from a cyclotron installed in The Institute of Physical and Chemical Research and 2 MeV electrons from an electron accelerator installed in JAERI Takasaki Radiation Chemistry Research Establishment.

A chamber, the scheme of which is shown in *Figure 2*, was specially constructed for proton irradiation. This chamber is characterized by scanning specimen against proton beam; the specimen, mounted on an aluminium rotor of 50 mm diameter, was rotated and moved repeatedly along the rotation axis. It was confirmed from the experiment using a cellulose triacetate (CTA) film dosimeter[23] that the specimen can be irradiated uniformly over an area of $157 \times 36\,\mathrm{mm}^2$, which is enough to measure tensile properties.

Specimens were irradiated under vacuum with a proton beam adjusted to 5 mm horizontally and 15 mm vertically. Since the range of protons with energy of 8.06 MeV was reported to be 74.78 mg cm^{-2} for polyethylene[24], 8 MeV protons have enough energy to pass through a polymer film of 100 μm thickness. The beam current passing through the specimen was monitored and the total charge was obtained by integrating the current. The beam current measured in this way agreed well with the value measured by using an aluminium Faraday cup (without a suppressor for secondary electrons). Although some error might be included in the measured beam current, because of the lack of a suppressor of secondary electrons and of change in charge density during passage through the film, no major problems were encountered in the dosimetry using the CTA dosimeter (125 μm thickness)[23].

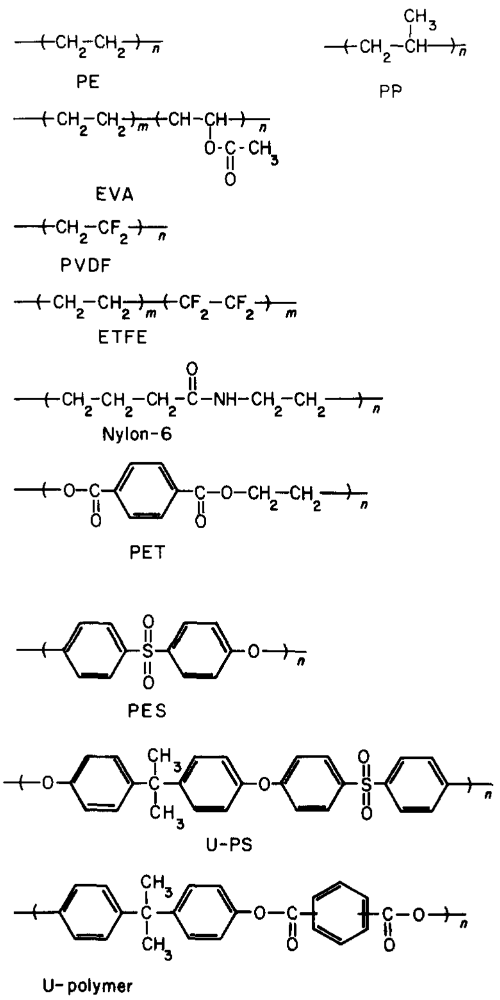

Figure 1 Chemical structures of polymers used

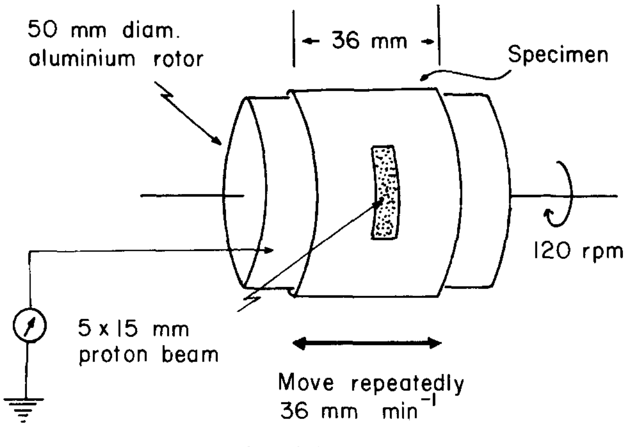

Figure 2 Schematic drawing of chamber for proton irradiation

Usually, the incident beam current was about 1 μA and the average fluence rate on a specimen of area 56.5 cm^2 was about 13 nC $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$. The temperature increase of the specimen during irradiation was monitored by a thermo-colour indicator attached to the rotor, and was confirmed to be less than 60°C.

Electron irradiation was carried out in a vessel equipped with gas flow and vacuum facilities. In general, the presence or absence of a radiation-induced oxidation reaction strongly affect degradation of the polymer, but the effects induced by irradiation in an inactive gas are regarded as the same as those in vacuum, so irradiation was carried out in a helium atmosphere. The electron fluence rate was 1.07 μC $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ and the dose rate was 25 kGy s^{-1}, which was measured by using the same CTA film dosimeter. Temperature increase of specimens during irradiation was prevented by the helium gas flow.

Evaluation of absorbed dose

Energy absorbed by materials (absorbed dose D) in the irradiation of charged particles is given by:

$$D = S \times Q \tag{1}$$

where S is the mass collision stopping power of the material for the incident ion and Q is the fluence. S is calculated from Bethe's equation[25]:

$$\begin{aligned} S &= (-\mathrm{d}E/\mathrm{d}x)/\rho \\ &= 0.3070Z(\rho/A)[\ln(2m_0v^2)/\langle I\rangle(1-\beta)-\beta^2]/\rho \end{aligned} \tag{2}$$

where ρ is density ($\mathrm{g\,cm}^{-3}$), Z and A are mean atomic number and mean atomic weight respectively of target materials, m_0 is rest mass of electron (amu), v is velocity of incident ion ($\mathrm{cm\,s}^{-1}$), $\beta = v/c$ (c is velocity of light) and $\langle I\rangle$ is mean excitation energy of medium (eV). The mean excitation energy $\langle I\rangle$ of each polymer was calculated from the excitation energy of each element constituting the polymers by using an additivity rule[25]:

$$\langle I\rangle = \left[\left(\sum_j w_j(Z_j/A_j)\ln I_j\right)\Big/\langle Z/A\rangle\right] \tag{3}$$

$$\langle Z/A\rangle = \sum_j w_j Z_j/A_j$$

where w_j, Z_j, A_j and I_j are fraction by weight, atomic number, atomic weight and mean excitation energy of the jth constituent, respectively. When the units of S and Q are MeV cm^2 g^{-1} and μC cm^{-2} respectively, D in equation (1) has units of kGy.

The absorbed dose (D_e) for polymers in electron irradiation was corrected as:

$$D_e = D_c(S_e \text{ of polymer})/(S_e \text{ of CTA}) \qquad (4)$$

where D_c is the dose measured by a CTA film dosimeter and S_e is the mass stopping power for electrons. S_e was calculated by the Seltzer and Berger method[26].

The stopping powers of the polymers used in this experiment for 8 MeV protons and 2 MeV electrons and the ratio of proton to electron stopping powers are summarized in *Table 1*.

Tensile tests

The tensile test was carried out at 25° with a cross-head speed of 200 mm min^{-1} on specimens in the form of an ASTM 1822 type dumbbell. The tensile strength at break and the ultimate elongation were determined and are represented by the average and standard deviation of six specimens.

RESULTS

Table 1 Stopping powers of polymers used in this work for 8 MeV protons and 2 MeV electrons

Polymer	Stopping power (MeV cm^2 g^{-1}) Proton	Electron	Ratio
PE	53.0	1.772	29.9
PP	53.0	1.773	29.9
PVDF	46.6	1.722	27.0
ETFE	46.7	1.771	27.1
EVA	52.3	1.771	29.5
Nylon-6	51.8	1.771	29.3
PET	50.1	1.776	28.2
PES	48.9	1.783	27.6
U-PS	49.6	1.778	27.9
U-polymer	50.4	1.775	28.4

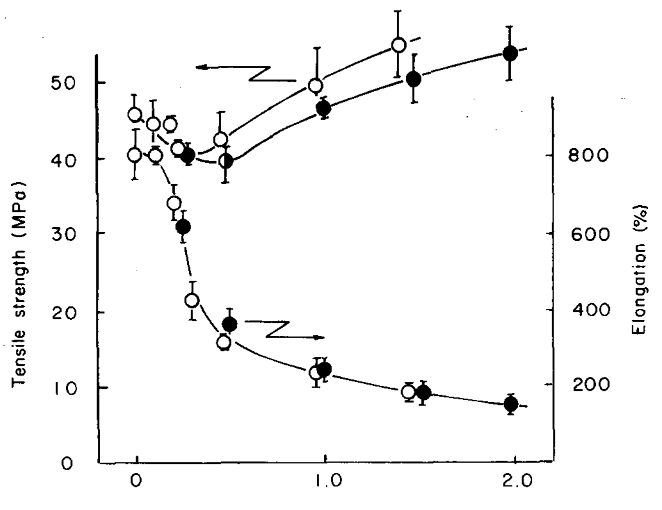

Figure 3 Changes in tensile properties of PE as a function of absorbed dose of protons (○) and electrons (●)

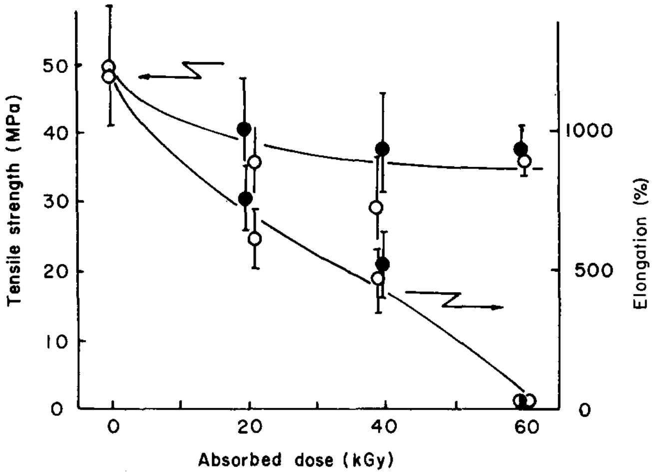

Figure 4 Changes in tensile properties of PP as a function of absorbed dose of (○) protons and (●) electrons

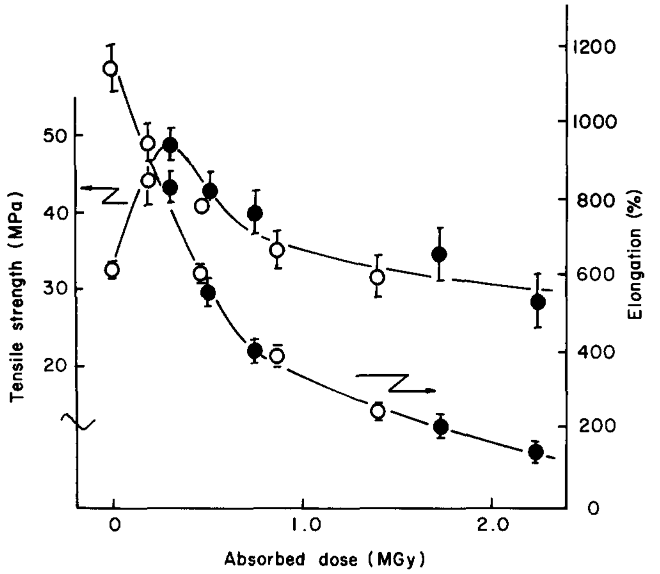

Figure 5 Changes in tensile properties of EVA as a function of absorbed dose of protons (○) and electrons (●)

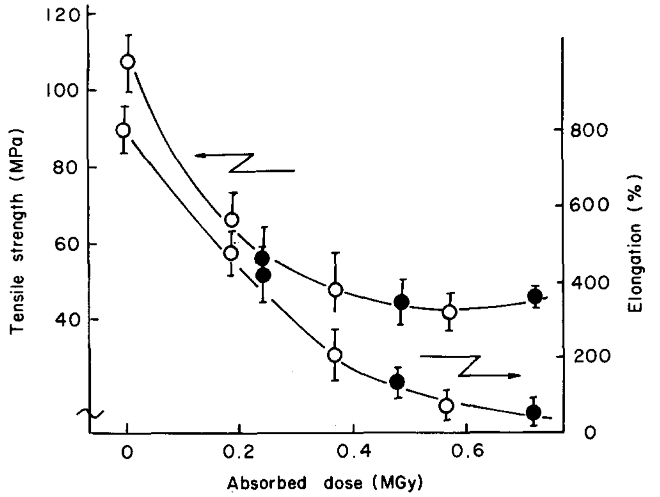

Figure 6 Changes in tensile properties of ETFE as a function of absorbed dose of protons (○) and electrons (●)

Figures 3–8 show the tensile strength at break and the ultimate elongation as a function of absorbed dose for PE, PP, EVA, PVDF, ETFE and nylon-6, respectively. The profiles of the dose dependence curves differ for each polymer; for instance, the tensile strengths of PE and ETFE decrease at once in the initial stage and then increase in the higher dose region, and that of EVA

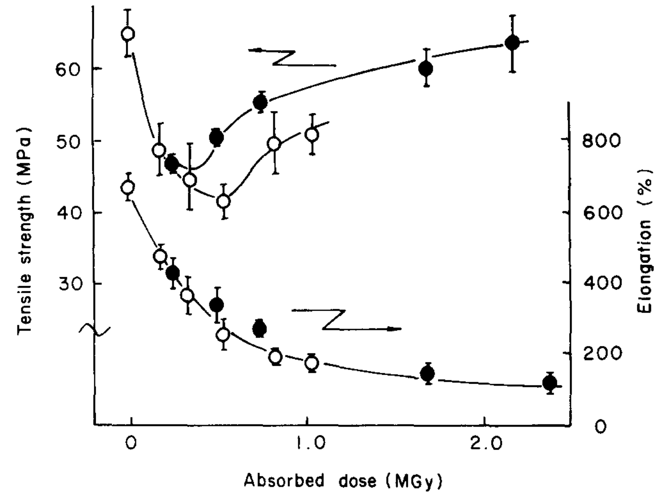

Figure 7 Changes in tensile properties of ETFE as a function of absorbed dose of protons (○) and electrons (●)

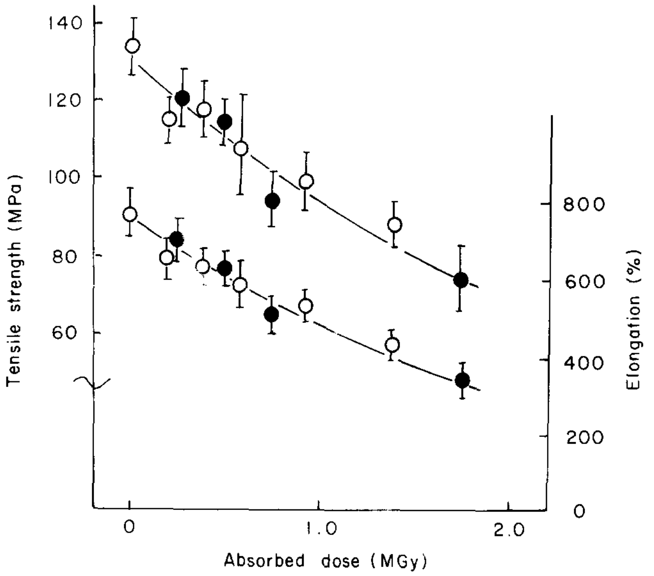

Figure 8 Changes in tensile properties of nylon-6 as a function of absorbed dose of protons (○) and electrons (●)

increases at once and then decreases with dose. Little or no differences are observed in the changes in the tensile parameters per dose between proton and electron irradiation in each polymer.

The changes in the tensile properties with dose for PET are shown in *Figure 9*. This polymer is composed of aliphatic and aromatic units. In this case, the decreasing rate of tensile strength with dose in proton irradiation can be regarded to be less than that in electron irradiation.

Figures 10–12 show the same relations for PES, U-PS and U-polymer, which are composed of only aromatic unit. In contrast to aliphatic polymers, the manner of changes in tensile parameters with dose differs between proton and electron irradiation, i.e. the rate of decrease in the strength and elongation with dose in proton irradiation is clearly less than that in electron irradiation.

DISCUSSION

As shown in *Table 1*, the stopping powers for 8 MeV protons of the polymers used in this work are 27–30 times higher than that for 2 MeV electrons. Thus the linear energy transfer (LET) of 8 MeV protons can be regarded as being about 30 times larger than that of 2 MeV electrons.

The following results were reported on the LET effects of liquids[27,28]: (1) in experiments for cyclohexane, the yields of C_6H_{10} and $C_{12}H_{22}$ decrease and that of H_2 increases with LET; (2) the conversion of Fe^{2+} to Fe^{3+} in a ferrous sulphate dosimeter decrease with LET[27]; and (3) in experiments for benzene[29], the *G*-value of disappearance of C_6H_6 increases with LET. These results were interpreted in terms of an increase in probability of recombination of radicals and/or excited molecules. Thus, the characteristic effects in irradiation by ions having high LET in a condensed phase are the high-density excitation along the track and the increase in the probability of recombination of excited species.

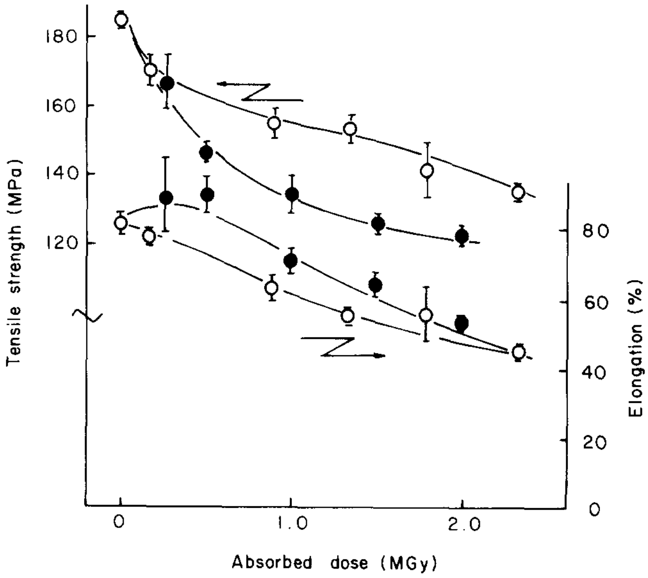

Figure 9 Changes in tensile properties of PET as a function of absorbed dose of protons (○) and electrons (●)

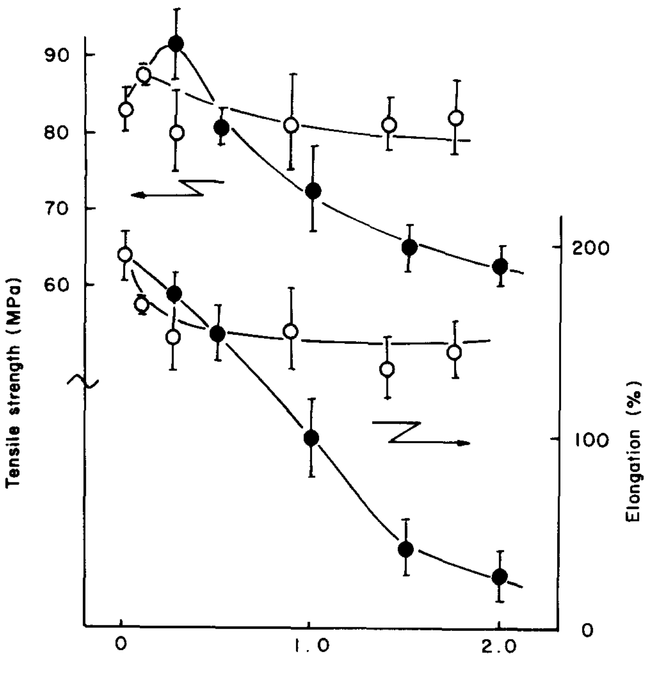

Figure 10 Changes in tensile properties of PES as a function of absorbed dose of protons (○) and electrons (●)

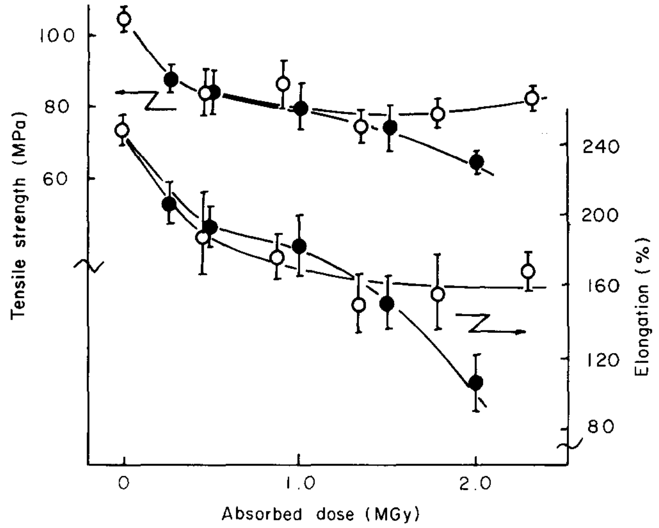

Figure 11 Changes in tensile properties of U-PS as a function of absorbed dose of protons (○) and electrons (●)

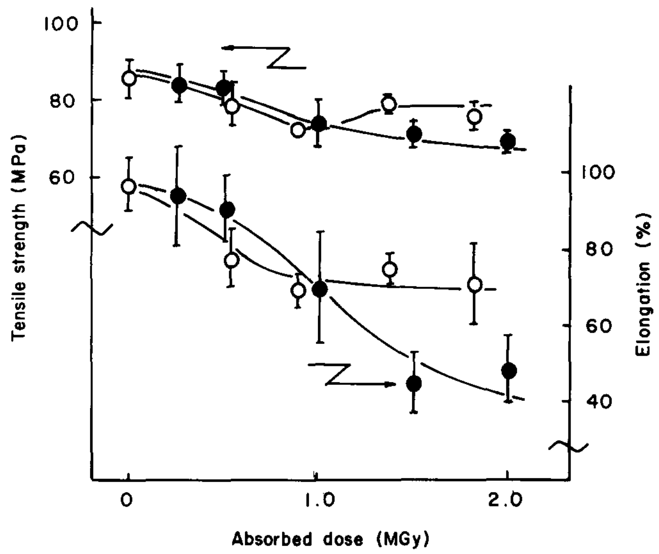

Figure 12 Changes in tensile properties of U-polymer as a function of absorbed dose of protons (○) and electrons (●)

Table 2 Fluences of 8 MeV protons and 2 MeV electrons that give the half value of the initial elongation for aliphatic polymers

	Fluence giving the half elongation ($\mu C\,cm^{-2}$)		
Polymer	Proton	Electron	Ratio
PE	6.0	185	30.8
PP	0.48	17	1.3
PVDF	4.3	105	24.8
ETFE	7.9	215	27.2
EVA	9.2	225	24.6
Nylon-6	28.9	646	22.4

The changes in the mechanical properties of polymers by ionizing radiation are ascribed mainly to chemical reactions like chain scission and/or formation of cross-links through excitation, ionization, formation of active species and their reaction. If the mechanism obtained in liquids could be applied to polymers, the radiation effects on mechanical properties are expected to alter with LET. In the case of polymers, however, the increase in recombination probability of the excited species with increase of their density is doubtful, because the diffusibility of active sites, which exist on less mobile polymer chains, would be considerably lower than that in low-molecular-weight liquid.

The results in aliphatic polymers demonstrate that there is little or no LET effect. *Table 2* shows the fluences giving the half value of the initial elongation in proton and electron irradiation for aliphatic polymers and their ratios. The ratios are in the range 23–30 and the values are comparable to the ratio of stopping powers. This result indicates also that the radiation effects depend on absorbed energy but scarcely depend on the method of energy deposition. The lower LET effects on mechanical properties in aliphatic polymers would result from the fact that the probability of recombination is hardly enhanced even though high-density excitation occurs.

In contrast, clear LET effects are observed in aromatic polymers. As reported previously[30], the glass transition of PES, U-PS and U-polymer shifts to low temperature with electron dose, and these polymers were classified as chain degradation type in electron irradiation. Coulter *et al.*[22] reported that the glass transition of U-PS shifts to higher temperature on 3 MeV proton irradiation, suggesting the formation of crosslinks. The less decreasing rate of the tensile parameters against proton dose (*Figures 9–12*) seems to result from an increase of recombination probability; however, it could not be interpreted only in terms of recombination of radicals formed finally, because the mobility of chains of aromatic polymers is as small as that in aliphatic polymers. It would be reasonable to consider that the process of energy deposition in the initial stage is different in aromatic and aliphatic compounds. In fact, different LET effects between cyclohexane and benzene were reported[27,28].

SUMMARY

Radiation effects induced by 8 MeV protons, for which the LET is about 30 times higher than that of 2 MeV electrons, on tensile properties of six kinds of aliphatic polymers and four kinds of aromatic polymers are compared with those caused by electron irradiation. Little or no LET effects are observed in the aliphatic polymers, but clear LET effects are observed in four types of aromatic polymers. Little or no LET effects would be the result of lower mobility of polymer chains, but accurate reasons for the appearance of high LET effects only in aromatic polymers cannot be given.

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