Degradation in tensile properties of aromatic polymers by electron beam irradiation

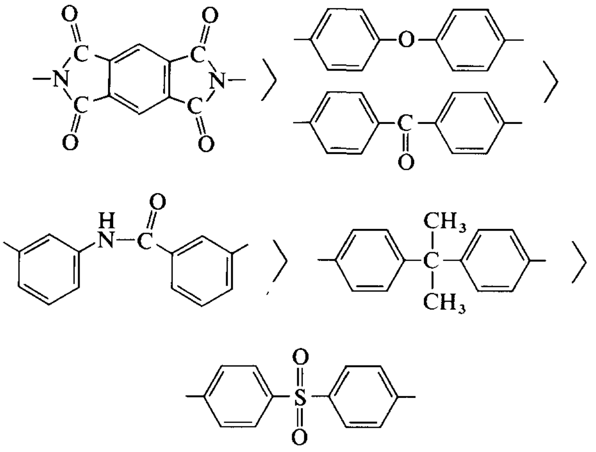
Tsuneo Sasuga, Naohiro Hayakawa, Kenzo Yoshida and Miyuki Hagiwara
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma 370-12, Japan

(*Received 2 April 1984; revised 14 May 1984*)

Electron beam irradiation effects of ten kinds of polymers containing various aromatic rings linked by functional groups in the main chain (aromatic polymer) were studied with reference to change in tensile properties. The polymers studied were polyimides 'Kapton H', and 'UPILEX', polyetherimide 'ULTEM', polyamides 'A-Film', and 'APH-50 (nomex type paper)', poly-ether-ether-ketone 'PEEK', polyarylate 'U-Polymer', polysulphones 'Udel-Polysulphone', and 'PES', and modified poly(phenylene oxide) 'NORYL'. Irradiation was carried out by use of electron beam at a dose rate of 5×10^3 Gy s^{-1} at room temperature. The elongation at break was the most severely influenced by the irradiation and it decreased with increasing dose. The order of radiation resistivity which was evaluated from the dose required for the elongation to become 50% and 20% of the initial value was as follows:

Polyimide > PEEK > polyamide > polyetherimide > polyarylate > polysulphone, poly(phenylene oxide)

Based on the above experimental results, the following order was proposed as for the radiation stability of the aromatic repeating units composing the main chain:



(Keywords: aromatic polymers; electron beam; tensile properties; degradation; aromatic repeating units; radiation stability)

INTRODUCTION

The development of polymers containing aromatic rings linked by various functional groups in the main chain (aromatic polymers) was extensively made during the 1970's to assist production of thermoresistant engineering plastics. Several of the aromatic polymers have already been employed in the high temperature apparatus, and their further growth and the production of other aromatic polymers are prospective. Because of the versatility, these polymers should be imported for use in the nuclear energy field. Radiation resistivity is a very important property for use in the radiation fields and the studies of the radiation effects on those polymers are necessary.

Polyimides such as Kapton and Vespel were extensively studied and reported having resistivity for γ rays and electron beam up to ~100 MGy of radiation[1,2]. Coltman *et al.*[3,4] and Takamura *et al.*[5-7] reported that these polymers have also an excellent resistivity under reactor irradiation. Several kinds of polysulphones were studied by O'Donnel *et al.*, Hinkley and Campbell, and Gillham *et al.* by measuring the solution viscosity[8,9], gas evaluation[10], fracture toughness[11] and by torsional blade analysis[12]. Studies on other aromatic polymers such as polyimide, poly(phenylene sulphide) and poly(phenylene oxide) are appeared in the series of work in CERN[13].

As mentioned above radiation effects of aromatic polymers have been studied on limited polymers and, furthermore, the radiation source, irradiation condition, and evaluation technique of damage differed. To obtain generalized knowledge for radiation effects of aromatic polymers, studies should be carried out using identical

0032-3861/85/071039-07$03.00

degradation condition and identical criterion of evaluation of damage for wide varieties of polymers. In this paper relative radiation resistivity was studied for ten kinds of aromatic polymers by electron beam irradiation in air at room temperature. Radiation damage was evaluated by measuring tensile properties.

EXPERIMENTAL

The polymers used in the experiment are as follows; polyamides 'Kapton' and 'UPILEX', polyetherimide 'ULTEM', polyamides 'A-Film' and 'APH-50 (nomex type aramide paper)', poly(ether ether ketone) 'PEEK', polysulphones 'Udel-Polysulphone', 'PES(polyethersulphone)', and modified poly(phenylene oxide) 'NORYL'. Their chemical structures are shown in *Figure 1*. These samples except NORYL contained no additives and were received in film forms of 100 to 200 micron thickness. Irradiation was carried out for the specimens shaped in JIS No. 4 dumbbell by electron beam with a dose rate of 5×10^3 Gy s^{-1} (for CTA film dosimeter; 2MeV, 1.5 mA) in air. To prevent rise of temperature of the specimens during irradiation, the were placed on a stainless steel plate which was cooled by flowing water. The temperature rise can be neglected, but the dose rate is slightly increased due to back scattering. In this paper, however, total dose is determined simply by dose rate (5×10^3 Gy s^{-1}) x irradiation time (s), because exact correction for the back scattering is rather difficult.

The tensile tests were carried out at 25°C with the cross head speed of 200 mm min^{-1}. The Young's modulus was obtained from the initial slope of the stress–strain curves (S–S curves), the yield strength was obtained from the maximum stress just after yielding, the tensile strength was obtained from the stress at break and the elongation at break was determined by dividing simply over all displacement by initial length of the dumbbell neck. These values were indicated by the mean value of 5 specimens and standard deviation.

RESULTS

Figures 2 and *3* show the typical S–S curves for Kapton and PEEK. The S–S curves of Kapton are typical, elongating without necking. The elongation at break and the tensile strength decrease and the Young's modulus tends to increase with dose. Polyimide UPILEX and polyamide paper APH-50 shows similar S–S curve without necking. The S–S curves of PEEK are typical ones elongating with necking and other polymers except Kapton, UPILEX, and APH-50 show necking also during elongation. The elongation at break and the tensile strength decrease with increasing dose, but the change in yield strength and Young's modulus are less pronounced.

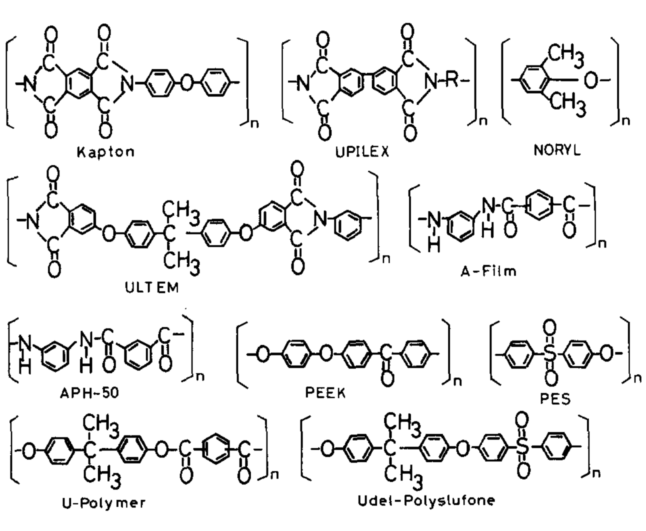


Figure 1 Chemical structures and commercial names of aromatic polymers

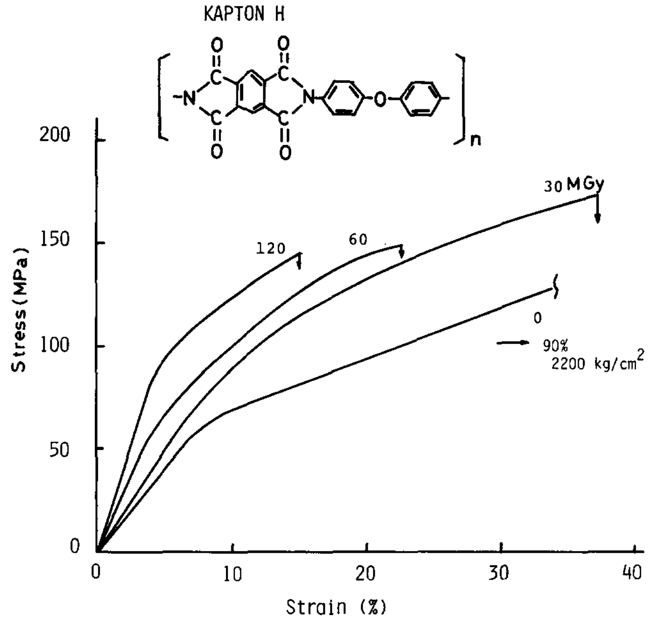


Figure 2 The stress–strain curves of polyimide 'Kapton' irradiated by various doses

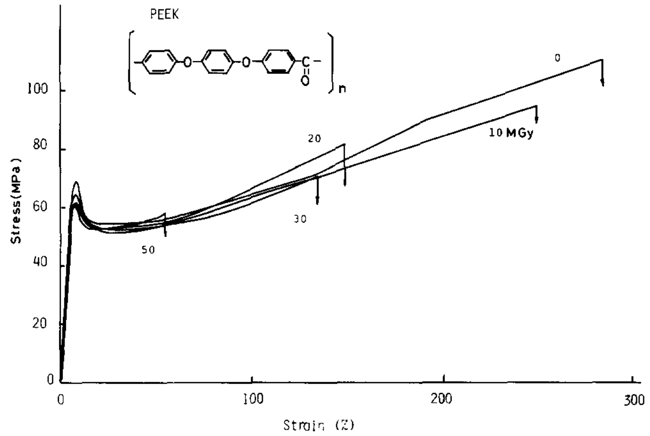


Figure 3 The stress–strain curves of non-crystalline PEEK irradiated by various doses

Table 1 shows the relation between the tensile parameters and dose for all polymers. *Figures 4*, *5 6* and *7* show the change in tensile parameters as a function of dose for Kapton, UPILEX, PEEK and Udel-Polysulphone. The error bars show the standard deviations. As shown in *Figure 4*, the tensile parameters of Kapton differ by the direction parallel to the direction of extrusion (MD) the tensile strength and Young's modulus are larger and the elongation at break is smaller than those elongated in the traverse direction of extrusion (TD). The differences in the properties by direction of elongation disappear above 50 MGy. *Figure 4* also shows that Kapton is a high radiation resistive polymer, since the residual elongation keeps about 10% of the initial value and being considerably flexible even after the irradiation of 120 MGy.

Table 1 Tensile properties of electron beam irradiated aromatic polymers

Sample	Dose (MGy)	Young's modulus (MPa)	Yield strength (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
Kapton 500H (TD)	0	$1.73\times10^3\pm78$		211.9±5.2	118±5
	10	$1.79\times10^3\pm96$		173.8±3.7	57±4
	30	$1.82\times10^3\pm130$		168.3±7.8	37±6
	60	$1.84\times10^3\pm82$		107.1±4.0	28±4
	90	$1.97\times10^3\pm94$		168.1±2.9	21±1
	120	$1.95\times10^3\pm92$		149.7±9.4	14±3
Kapton 500H (MD)	0	$1.83\times10^4\pm71$		224.2±9.9	90±10
	10	$1.93\times10^3\pm37$		192.2±3.4	51±3
	30	$2.02\times10^3\pm60$		179.4±3.9	25±2
	60	$2.02\times10^3\pm57$		186.7±2.4	24±1
	90	$2.04\times10^3\pm164$		178.8±10.4	19±3
	120	$1.97\times10^3\pm57$		155.5±14.2	14±4
UPILEX	0	$2.09\times10^3\pm40$	154.4±1.0	237.8±12.4	96±7
	10	$2.06\times10^3\pm76$	150.9±1.5	213.9±6.2	81±4
	20	$2.19\times10^3\pm55$	153.2±1.4	198.2±4.3	64±3
	50	$2.06\times10^3\pm91$		156.3±3.3	26±8
	60	$2.05\times10^3\pm116$		156.7±2.1	20±2
	90	$2.02\times10^3\pm100$		154.3±1.7	14±1
	120	$2.08\times10^3\pm164$		148.0±1.4	12±2
ULTEM	0	$1.45\times10^3\pm35$	121.7±1.7	135.1±9.1	161±20
	3	$1.58\times10^3\pm100$	116.0±4.3	103.2±4.3	42±20
	5	$1.59\times10^3\pm72$	114.3±2.5	99.9±2.0	26±10
	7	$1.64\times10^3\pm102$	116.1±3.5	97.2±3.0	25±21
	10	$1.35\times10^3\pm96$	107.3±1.5	92.1±2.5	16±5
	20	$1.53\times10^3\pm22$	107.6±1.6		8±1
A-Film	0	$2.29\times10^3\pm59$	125.6±1.1	147.9±1.2	186±7
	10	$2.36\times10^3\pm180$	133.7±2.1	139.1±17.7	141±50
	20	$2.38\times10^3\pm115$	135.3±2.3	115.7±12.2	61±37
	30	$2.19\times10^3\pm87$	120.3±1.1	94.7±1.1	22±6
	50	$1.14\times10^3\pm85$	71.6±1.4	60.2±6.1	13±3
A-Paper (TD)	0	$1.26\times10^3\pm189$		62.6±6.2	13±2
	10	$1.23\times10^3\pm170$		55.5±1.5	7±1
	20	$1.33\times10^3\pm77$		55.8±1.1	6±1
	30	$1.64\times10^3\pm144$		40.2±4.4	3±0
A-Paper (MD)	0	$1.78\times10^3\pm168$		96.3±7.1	15±2
	10	$1.50\times10^3\pm135$		79.9±4.8	11±3
	20	$1.72\times10^3\pm94$		79.1±1.3	6±1
	30	$1.88\times10^3\pm176$		61.5±7.1	3±1
PEEK (non-cryst.)	0	$1.17\times10^3\pm75$	77.3±1.2	132.3±13.9	296±33
	10	$1.20\times10^3\pm23$	67.4±0.8	105.4±5.1	231±12
	20	$1.27\times10^3\pm39$	65.0±1.9	89.0±1.2	142±6
	30	$1.36\times10^3\pm87$	65.3±3.1	75.8±4.0	99±12
	50	$1.42\times10^3\pm20$	61.4±3.6	57.5±4.0	52±7
PEEK (cryst.)	0	$1.37\times10^3\pm70$	97.4±1.7	97.0±8.0	175±33
	5	$1.37\times10^3\pm88$	98.6±1.8	91.7±3.3	120±22
	10	$1.53\times10^3\pm84$	95.0±0.5	84.3±2.6	73±33
	20	$1.48\times10^3\pm83$	93.4±1.2	85.0±1.6	49±8
	30	$1.53\times10^3\pm129$	88.9±5.8	83.0±5.6	40±7
	50	$1.35\times10^3\pm287$	90.7±1.0	84.8±1.4	26±4
U-Polymer	0	$1.06\times10^3\pm32$	73.7±1.1	75.8±2.0	88±10
	0.5	$1.12\times10^3\pm80$	72.5±0.7	66.7±1.7	36±14
	1	$1.22\times10^3\pm43$	72.2±0.7	66.3±1.7	34±5
	2	$1.26\times10^3\pm49$	69.3±2.5	67.5±1.9	14±5
	5	$1.27\times10^3\pm74$		60.5±13.5	7±3
Udel-Polysulphone	0	$1.02\times10^3\pm76$	84.2±1.2	84.8±2.0	235±4
	0.25	$1.10\times10^3\pm34$	76.6±0.8	82.3±2.1	211±5
	0.5	$1.19\times10^3\pm38$	75.1±1.0	73.7±1.9	171±8
	1	$1.31\times10^3\pm29$	76.7±0.9	59.7±1.6	42±11
	1.5	$1.29\times10^3\pm70$	75.8±0.5	58.2±0.6	20±8
PES	0	$1.36\times10^3\pm82$	89.8±1.3	81.6±6.9	175±5
	0.25	$1.28\times10^3\pm60$	88.1±1.0	80.3±5.9	148±29
	0.5	$1.37\times10^3\pm87$	87.7±1.6	75.2±3.9	110±26
	1	$1.36\times10^3\pm115$	87.0±0.6	73.6±9.3	23±11
	1.5	$1.45\times10^3\pm68$	88.6±2.0	68.4±4.6	15±4

Table 1 (*continued*)

Sample	Dose (MGy)	Young's modulus (MPa)	Yield strength (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
NORYL (modified PPO)	0	$1.28\times10^3\pm77$	71.5 ± 3.7	59.1 ± 2.9	31 ± 10
	0.25	$1.23\times10^3\pm37$	71.3 ± 2.4	56.2 ± 1.9	22 ± 2
	0.5	$1.30\times10^3\pm69$	73.1 ± 2.0	57.8 ± 1.9	22 ± 4
	1	$1.32\times10^3\pm71$	75.5 ± 4.3	63.4 ± 4.8	14 ± 2
	1.5	$1.34\times10^3\pm23$		76.1 ± 9.2	8 ± 1

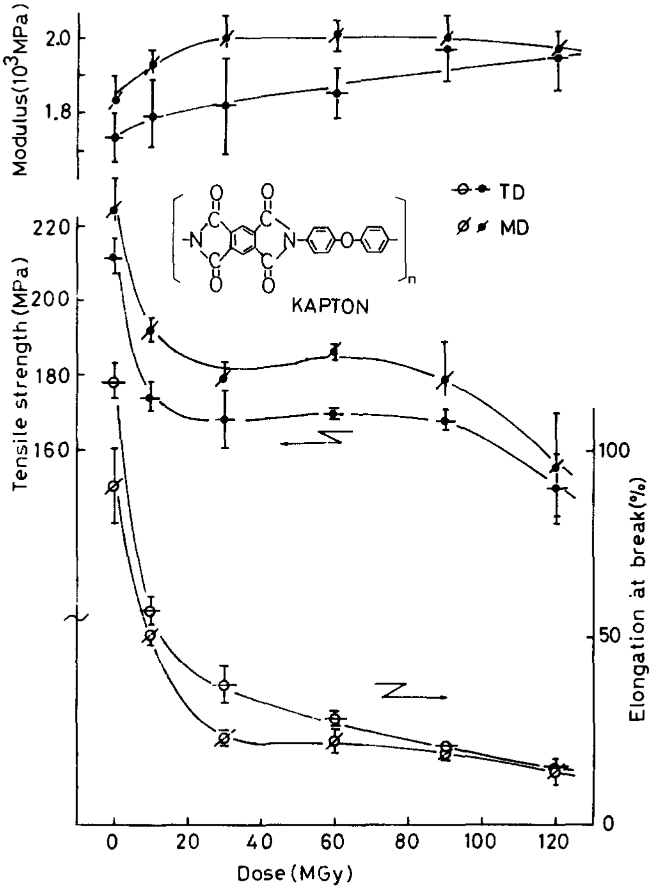


Figure 4 The plot of tensile parameters as a function of dose for Kapton

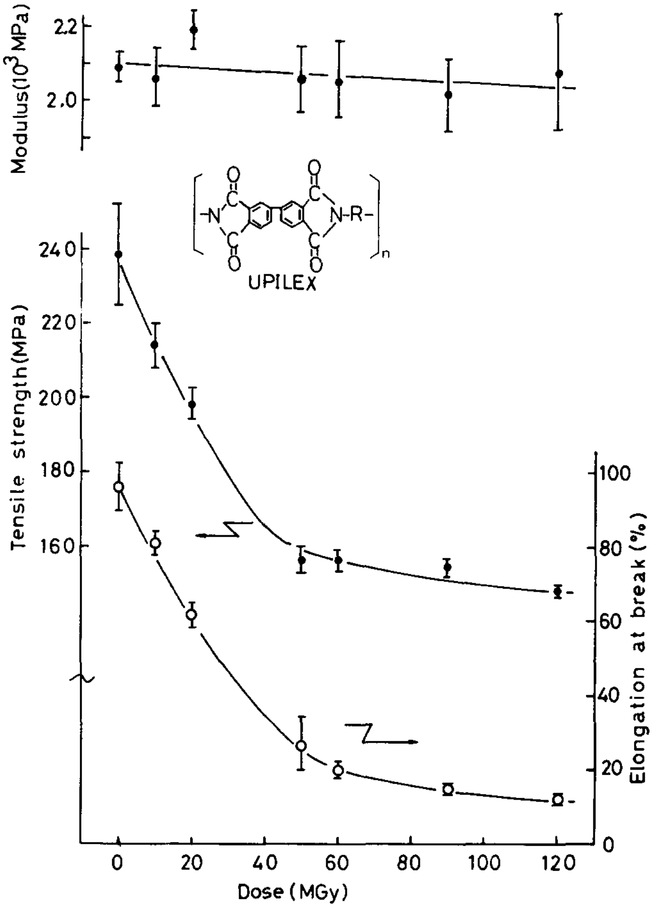


Figure 5 The plots of tensile parameters as a function of dose for polyimide 'UPILEX'

In the case of UPILEX, the tensile parameters are scarcely affected by the direction of elongation. *Figure 5* shows the change in the tensile parameters of UPILEX with dose. The elongation at break and the tensile strength decrease with increasing dose, but their decrements are smaller compared with those in the case of Kapton at low doses less than 50 MGy. UPILEX is more radiation stable than Kapton in that dose range.

Figure 6 shows the results obtained for PEEK. It becomes non-crystalline when quenched from the melting point (~320°C), but can crystallize when annealed above 180°C. In *Figure 6* the curves noted (a) are for non-crystalline PEEK and the ones noted (c) are for the crystalline PEEK which was annealed at 200°C for 30 min. The degree of crystallinity is ~15%. The Young's modulus and tensile strength increase and the elongation at break decreases with crystallization. This Figure shows that the decrement of elongation by irradiation for the crystalline PEEK is larger than for the non-crystalline PEEK. The yield strength is changed slightly by radiation compared with elongation at break and the tensile strength.

Figure 7 shows the relation between the tensile parameters and dose for Udel-Polysulphone. The decrease in elongation occurs substantially with a lower dose by about two orders than for polyimide and PEEK. The tensile strength decreases similar to the elongation with dose, but the yield strength becomes almost unaffected after a slight decrease at low doses.

DISCUSSION

The aromatic polymers subjected in this experiment are known to be very stable for heat and ultraviolet rays, but their stability against electron beam differs very widely with their chemical structures. In general, the change in physical properties of the polymer is brought about by the change, not only in the first order structure, but in a higher order structure such as the presence or absence of crystals. For instance, the tensile properties of the crystalline PEEK differ from those of the non-crystalline PEEK. The strength and modulus increase and the elongation decreases with crystallization (*Figure 6*). The molecular

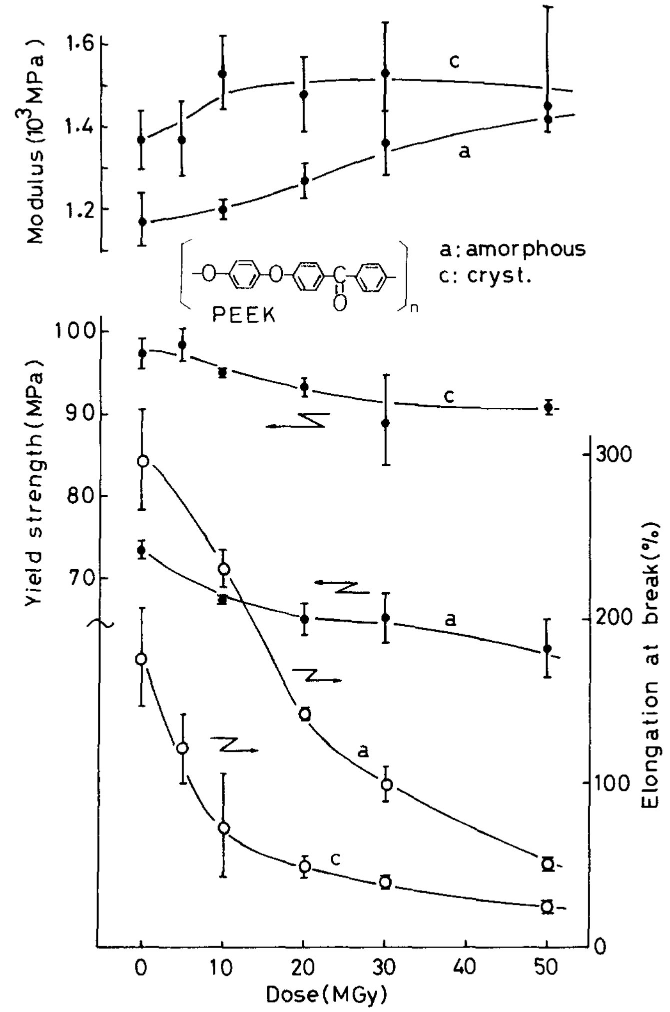


Figure 6 The plots of tensile parameters as a function of dose for non-crystalline PEEK (a) and crystalline PEEK (c); degree of crystallinity is about 15%

packing and molecular motion differ in non-crystalline and crystalline regions. Radiation effects should also be affected by the absence or presence of crystals, because the conformation and the molecular motion may have a large influence on reactivity of the active species produced by irradiation. The difference in radiation effects between the non-crystalline and the crystalline PEEK supports the above discussion. Therefore, the radiation stability of various polymer structures should be compared under the condition that the effects of crystallinity can be excluded. All of the polymers studied in this paper are non-crystalline except crystalline PEEK, so that the radiation stability of aromatic repeating units composing polymer chain can be estimated by the comparison between the mechanical radiation resistivity and the chemical structure for various polymers, as long as crystallization does not occur during irradiation.

Among the tensile parameters the change in elongation by irradiation is the most conspicuous. The decrease in elongation indicates decrease in flexibility and increase in brittleness. Therefore, the degree of mechanical deterioration of a material can be evaluated by decrease in elongation. *Figure 8* shows the residual elongation of 50% and 20% of the initial value as a function of dose for each polymer. The radiation stability of the units which make up the main chain is estimated by comparison of chemical structures and the residual elongation as follows:

(1) The polyimide such as Kapton and UPILEX show extensive radiation resistivity, indicating that aromatic imide ring has excellent radiation stability.

(2) The two aromatic polyamides, A-Film and APH-50, show relatively high stability for radiation, so the aromatic amide is a highly resistive structure for radiation.

(3) Non-crystalline PEEK shows also very high radiation resistivity, indicating that the aromatic ether and aromatic ketone are stable under irradiation.

(4) The polyetherimide ULTEM shows radiation resistivity of only several MGy, although it consists of the radiation resistive imide ring and aromatic ether. Similarly, the polyarylate U-Polymer, in spite of containing the stable aromatic ether and ester, shows low radiation resistivity. These two polymers contain bis-phenol A group in the main chain. It is considered that the bis-phenol A group is a low radiation stable structure.

(5) Since the two polysulphones show very low resistivity, the aromatic sulphone group does not have high radiation stability.

(6) The modified poly(phenylene oxide) NORYL shows low radiation resistivity. The phenylene oxide unit cannot be considered a weak structure for radiation on the analogy with the case of aromatic ketone and ether. The modification, by blending with polystyrene for example, may weaken the radiation stability of this polymer.

From the comparison between structure and radiation resistivity of polymer, we propose the order of radiation stability of units in polymer chain as follows:

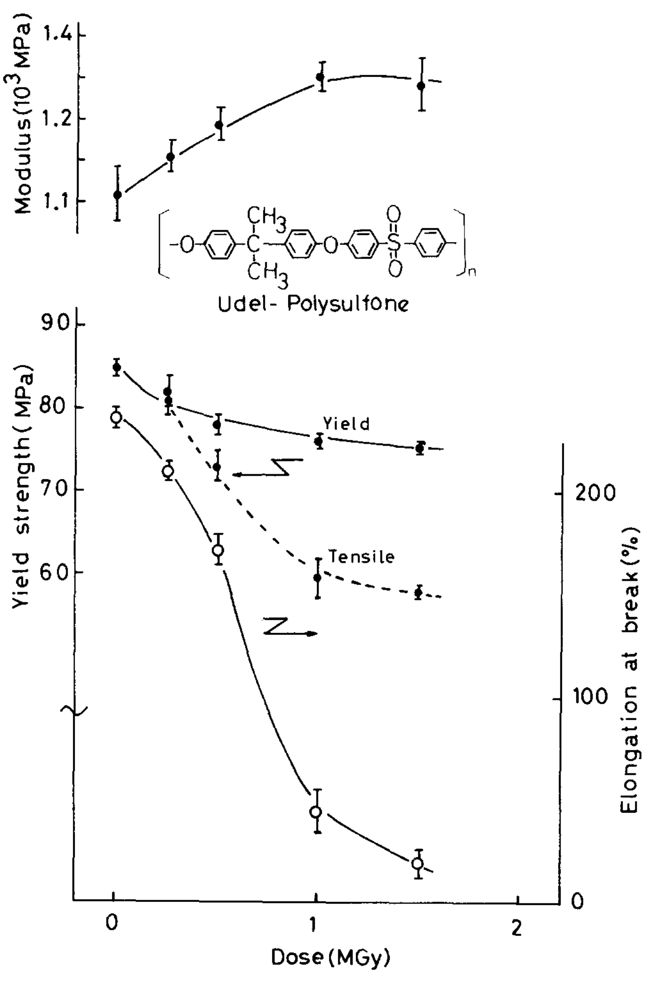


Figure 7 The plots of tensile parameters as a function of dose for Udel-Polysulphone

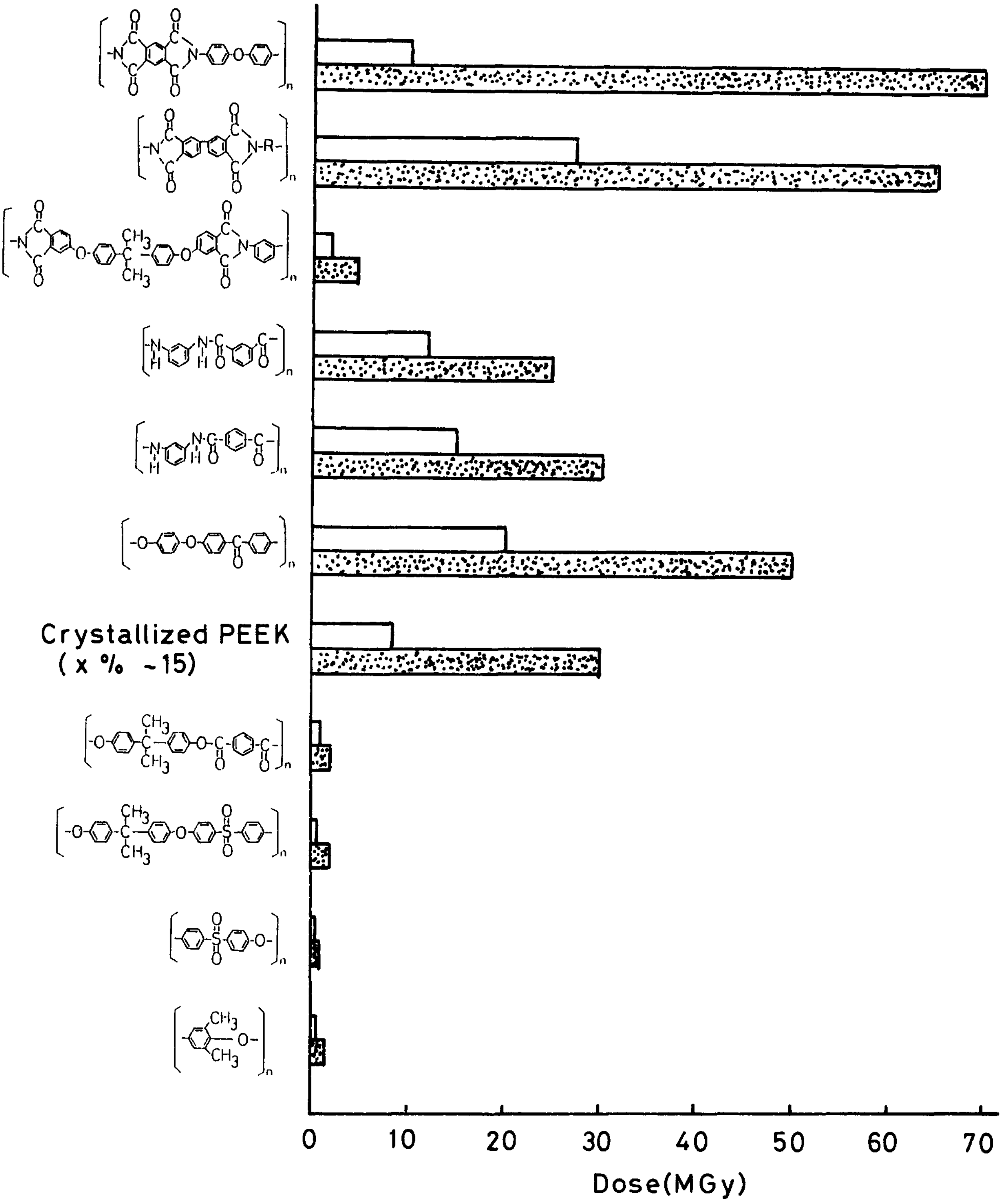
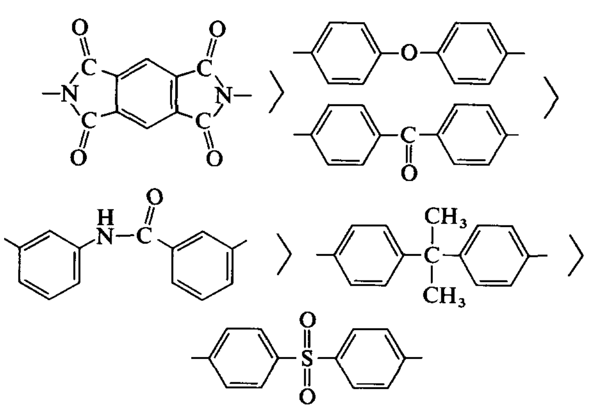


Figure 8 The relation between chemical structures and residual elongation; □ 50% of the initial value and ▨ 20% of the initial value



The order of stability is obtained for the irradiation of high dose rate electron beam in air. In the case of very high dose rate irradiation oxidation occurs only at the surface, since the radiation-induced oxidation is controlled by diffusion of oxygen. Therefore, this irradiation condition is regarded as similar to the irradiation *in vacuo*. In the case of oxidative irradiation, for example irradiation with low dose rate in air, the above stability order will probably change.

We have discussed the radiation stability based on change in tensile properties. The decrease of elongation also occurs by chain scission and crosslinking. It was reported for polysulphones that the chain scission occurs by γ irradiation in air and that both chain scission and crosslinking occur simultaneously *in vacuo*. Yoda pointed out recently the appearance of structure inhibiting crystallization upon electron beam irradiation to non-crystalline PEEK[14]. However, the information on the radiation chemical reaction for the other aromatic polymers is very limited. Studies on this subject are being carried out and the results will be reported in the near future.

ACKNOWLEDGEMENT

The authors thank Toray Co. Ltd., Sumitomo Kagaku Kogyo Co. Ltd., Nissan Kagaku Kogyo Co. Ltd., Uniticka Co. Ltd., and EPL Co. Ltd., for supplying polymer films.

REFERENCES

1 Du Pont, Information 'Kapton'

2 Hanks, C. L. and Hamman, D. J. 'Radiation Effects Design Hand Book', section 3, NASA-CR-1787 (1971)

3 Guess, J. F., Boom, R. W., Coltman, Jr., R. R. and Sekula, S. T. 'A survey of Radiation Damage Effects in Superconducting Magnet Comonents and Systems', ORNL/TM-1587 (1975)

4 Coltman, Jr., R. R., Kalabunde, C. E., Kernohan, R. H. and Long, C. 'Radiation Effects on Organic Insulators for Superconducting Magnets', ORNL/TM-7077 (1979)

5 Kato, T. and Takamura, S. *Teionkogaku* 1978, **13**, 243

6 Kato, T. and Takamura, S. *ibid.* 1979, **14**, 179

7 Kato, T. and Takamura, S. *ibid.* 1980, **15**, 173

8 Brown, J. R. and O'Donnel, J. H. *J. Polym. Sci., Part B* 1970, **8**, 121

9 Brown, J. R. and O'Donnel, J. H. *J. Appl. Polym. Sci.* 1975, **19**, 405

10 Brown, J. R. and O'Donnel, J. H. *J. Appl. Polym. Sci.* 1979, **23**, 2763

11 Hinkley, J. A. and Campbell, F. J. *J. Mater. Sci. Lett.* 1983, 276

12 Gillham, J. K., Pezdirtz, G. F. and Epps, L. *J. Macromol. Sci.-Chem.* 1969, **A3(6)**, 1183

13 Deynel, P., Mairer, P. and Schenbaher, H. 'Compilation of Radiation Damage Test Data Part II', 'Thermosetting and thermoplastic resins', CERN (1979)

14 Yoda, O. *Polymer* 1984, (*Commun.*) **25**, 238