2. Irradiation Facilities

2.1 *A Typical R&D Center on Radiation Processing in China

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INTRODUCTION

The industrial application of radiation processing has been growing rapidly in China since 1980's in such fields as manufacturing radiation crosslinked heat shrinkable materials, radiation crosslinked wire and cables, sterilization of medical products and so on. Changchun Institute of Applied Chemistry(CIAC), as one of the earliest organizations in which fundamental research work on radiation polymer chemistry was carried out, play a major role for R & D of radiation processing of polymers in China and nowadays has owned the largest enterprise of manufacturing radiation crosslinked heat shrinkable materials in China. The R & D activities at CIAC can be said to be very typical in China from which it can be seen how a chinese research institute transfer its results of fundamental research work into large scale production.

FUNDAMENTAL RESEARCH WORK

In the bigining of 60's , to meet the needs of our country and caught up with the rapid development of radiation chemistry in the world, some theoretical research work on radiation polymer chemistry was carried out in CIAC and then a 200,00 ci Co-60 source was the only radiation source by which most of research work was performed and thus this also constitutes one of characteristics of our current manufacturing, that is, most of radiation is performed through γ rays.

1. Radiation modification of fluoropolymers

Fluoropolymers, owing to their superior high temperature and chemical resistance, are widely used in some special fields. The marked weakness of them such as the sensitivity to high energy radiation and creeping of PTFE and the cracking of FEP, however, limit their application in some fields to a great extent. And thus we tried to solve the above problems by way of radiation crosslinking.

For FEP it was reported that it could be crosslinked by radiation performed above its glass transition temperature(1) . Owing to the

unavailablness of suitable solvent for FEP, the characterization of crosslinked polymer, however, was thought to be very difficult to conducted then . After carefully selection it was finally found in our laborotary that fluoro-chloro oil(oligmer of trifluoro chloro ethylene) could dissolve FEP at high temperature which made it possible to get the fraction of crosslinked part in irradiated FEP. On the basis of thus obtained sol data we calculated gelation dose and concerned parameters by using Charlesby - Pinner equation. Table 1 lists the obtained results.

As we all know that PTFE had been taken as typical radiation degradative polymer in all previous literatures and its radiation crosslinking was thought to be impossible. The observation of the fact that radiation stability of PTFE is increased upon raising irradiation temperature,however, encourage us to explore the possibility to crosslink the polymer by radiation. After many year's exploration, we finally found a very strict condition in 1980's only under which PTFE could be crosslinked by radiation. The finding of the condition resulted from an accidental phenomenon observed in an unsuccessful experiment in which we irradiated PTFE around 300 ℃ in vacuo. Then owing to the unevenness of temperature distribution in heater, irradiated PTFE sheets were found to appear semi- transparent in middle part caused by locally overheat and white color in two end of sheet as usual , the unusual hardness and strength of the semi-transparent part made us deeply convince that PTFE was crosslinked there. After further detailed work the crosslinking condition of PTFE was discovered, that is: 0.2 - 1 Mrad at 330 - 340 ℃ and in vacuo. Crosslinked PTFE was found to gain a great improvement in both mechanical properties and radiation stability as shown in figures 1- 4 which overcomes the creeping properties of PTFE.

2. Modification of Charlesby - Pinner equation

Charlesby - Pinner eqation is a basic one to describing relationship of sol fraction to irradiation dose from which we can get many important parameters concerning with crosslinking of polymers. During application, however, it was found that for certain polymers such as those having too rigid or soft polymer chains, the relation between $(s + s^{1/2})$ and $1/R$ will be nonlinear. On the basis of large number of experimental work and summarizing previous lectures, we finally presented a eqation which introduce a parameter β concerning with glass transition temperature Tg and internal rotating steric factor σ of polymer.

$$R(S + S^{1/2}) = 1/q_o U_r + \alpha_o R^{\beta}/q_o$$

$$\beta = 0.002Tg + 0.206$$

$$Tg = A(\alpha - a)$$

This equation is applicable to most of polymer systems.

3. Radiation grafting for preparing functional materials

(1) Radiation grafting palladium – acrylonitrile complex on inorganic compound to prepare polymer catalyst and thus obtained catalyst has higher active hydrogenation and better antitoxic than that obtain by chemical method.

(2) Radiation grafting of polymer metrix to prepare ionic polymer sensor – Ionic Selected Electrode(ISE)

i. Electrode for Cl^- & NO_3^- ions

Concerning property parameters:

Slope (mv/log C)	*58*
Detection concentration(M)	$8\times10^{-1} \sim 5\times10^{-6}$
PH region	*4 ~ 9.5*
Stability (mv/8hr)	*±0.9*
Internal resistance(Ω)	*⟨ 25*
Life time (month)	*⟩ 4*
Respond time (second)	*⟨ 10*

ii. Gadolinium ISE sensor – functional polymer active material

Slope of electrode	*52 ~ 59 mv/log C*
Detection limit	3.2×10^{-6} *M*

(3) Radiation grafting of acrylic acid on EVA to increase the hydrophilicity of grafted polymers.

4. Radiation crosslinking of polymer blends

The regularity of radiation crosslinking of polymer blends were investigated. These system include LDPE/EVA, LDPE/CPE, PMMA/PEO, PDMVS/LDPE and so on. Among them PMMA/PEO blend was found to be most interested which indicated that PMMA, a radiation degradative polymer, can be crosslinked in such a blend system in the dose range of 1 – 20 Mrad and composition of PMMA being 30 – 70%. The crosslinking degree of PMMA was found to be the largest for blend containing 70% PMMA.

5. The Effect of antioxidant on radiation crosslinking of polymer

Antioxidant was reported to affect radiation crosslinking of polymers owing to its absorption radiation energies and scavenging radiation induced radicals. The effect of structure and varieties of varying antioxidants on crosslinking process and changes in their stabilizing activities after exposure to radiation was examined which showed that for antioxidant examined in our work the activities of antioxidant was not affected by radiation ; the inhibitory effect of antioxidant on crosslinking of LDPE was not dependent on the concentration of antioxidant in the range of 0.5 - 2 phr and the post irradiation effect of LDPE was observed to be greatly inhibited by the presence of antioxidant.

APPLIED RESEARCH WORK

In the end of 70's to meet the needs of industrial division we set up a pilot factory in Jilin Radiation Chemistry Institue to manufacture EB crosslinked heat shrinkable tubings in a small scale. In the middle of 80's , required by the power department, we successfully developed 10- 35 KV radiation crosslinked power cable termination and set up a heat shrinkable material factory which belongs to CIAC. After that we developed varieties of heat shrinkable tubings, irregular shape heat shrinkable articles, heat shrinkable sheet and sleeves for bus bar prot ection, heat shrinkable sheet for communication cable joint and cap for the end protection of cable. Besides that we also developed varieties of chemical formulations of radiation crosslinked wire and cables including 6. 6 KV cable for airport runway; 105 ℃ grade high voltage wire for color TV; 125 ℃ grade flame retardant wire; non-halogen low smoke flame retardant wire and cables; 10 KV aerial cables , oil resistant cables for locomotive and heat shrinkable sleeves for pipe joint protection.

THE DEVELOPMENT OF RADIATION PROCESSING AT CIAC

The Heat Shrinkable Materials Factory of CIAC was established at 1987 when eight persions from research laboratory began to manufacture power cable accessories and heat shrinkable tubings with a 600,00 Ci Co- 60 source. With the rapid development of Chinese economy the radiation processing at CIAC has been growing at high speed. Today CIAC has owned 7 joint-venture branch factories spreaded in Shenzheng, Beijing, Shanghai, Xinjiang ,Nanjing,Xian and Shijiazhuang and 16 sales company all over China. The heat shrinkable products manufactured in these factories have occupied more than half of the market in China and some of them have been exported to Southeast Asia. Now it can be said that CIAC has become the largest R & D center of radiation processing in China. In March of this year a 1. 5 Mev electron accelerator

imported from Russia was put into operation and the problem of radiation ability being insufficient that CIAC met in past years is expected to solved, which lay a good foundation for the more rapid development of radiation processing at CIAC. The figures below give a quantitative description of the development of radiation processing at CIAC.

REFERENCE

(1) Bowers, G. H. and Lovejoy, E. R. Industrial & Engineering Chemistry Products Research & Development 1962, 1, 89

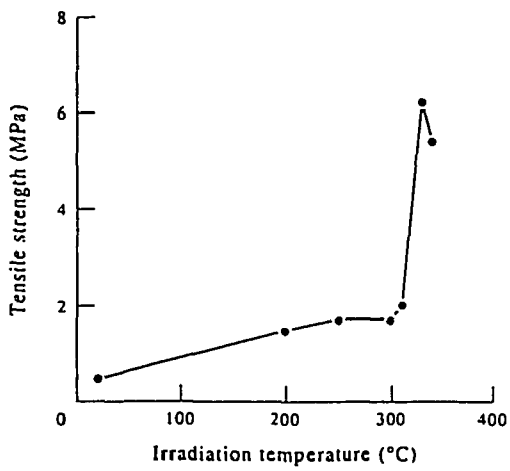


Fig. 1. Tensile strength at 200 C of PTFE absorbed 20 kGy

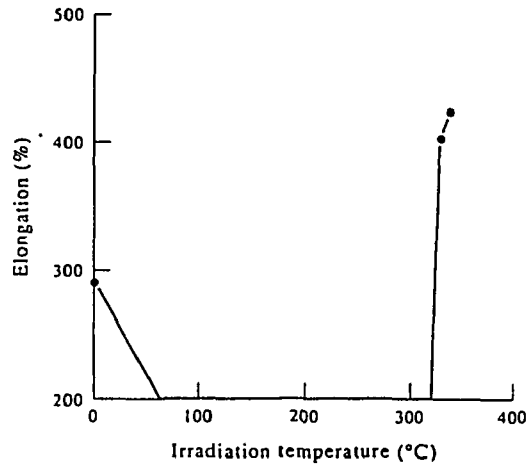


Fig 2. Elongation at 200°C of PTFE absorbed 20 kGy.

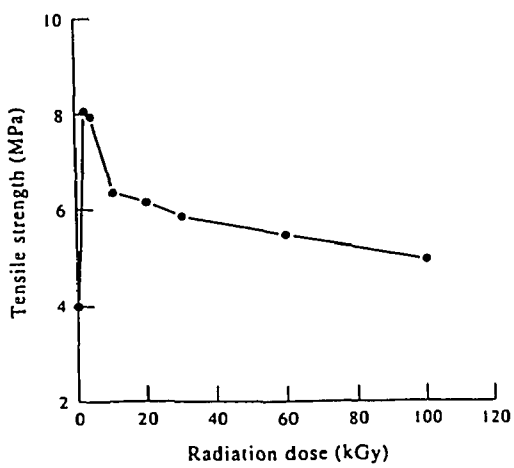


Fig. 3. Effect of dose on tensile strength at 200°C of PTFE irradiated at 330°C.

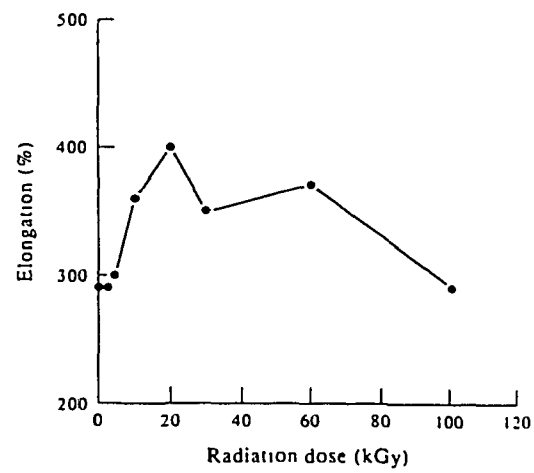


Fig. 4. Effect of dose on elongation at 200°C of PTFE irradiated at 330°C.

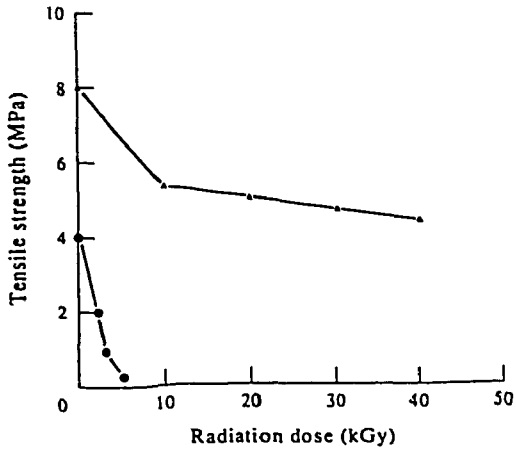


Fig. 5. Effect of aging dose on tensile strength at 200°C of PTFE. —●—, Control PTFE; —▲—, crosslinked PTFE.

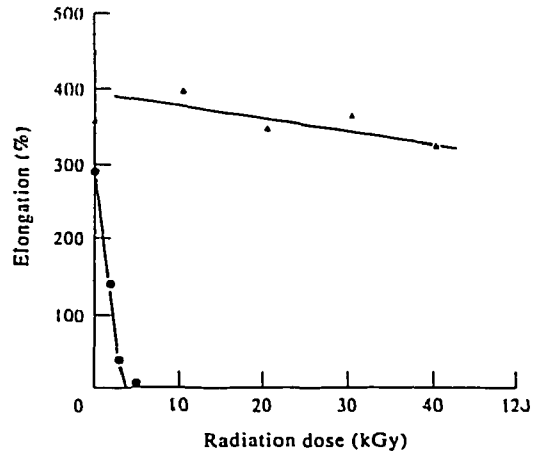


Fig. 6. Effect of aging dose on elongation at 200°C of PTFE. —●—, Control PTFE; —▲—, crosslinked PTFE.

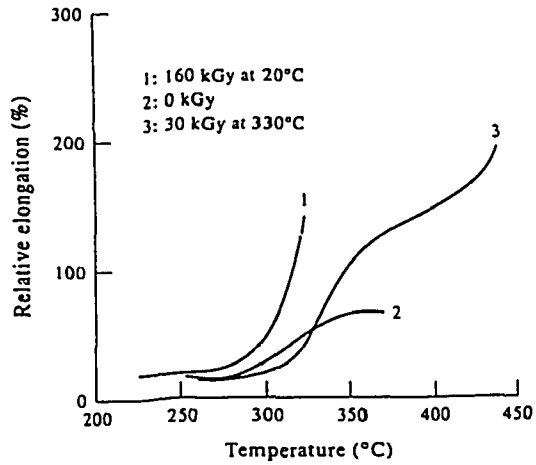


Fig. 7. Effect of radiation on TMA curves of PTFE.

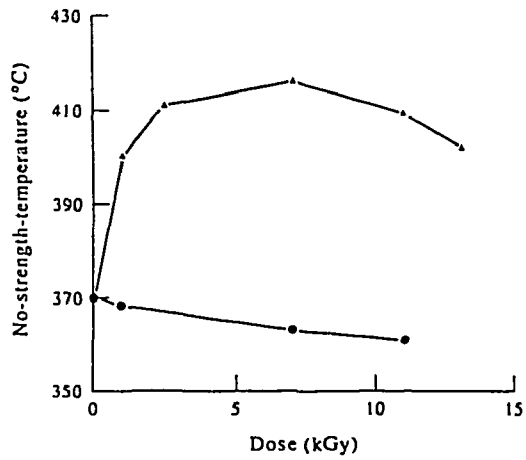


Fig. 8. Effect of radiation on NST of PTFE. —●—, Control PTFE; —▲—, crosslinked PTFE.

Table 1 Values of p_0/q_0 and gelation dose of FEP irradiated at different temperatures

Irradiation temperature (°C)	p_0/q_0	Gelation dose (Mrad)
150	1.35	12.3
210	0.85	10.0
220	0.80	8.0
240	0.42	2.5

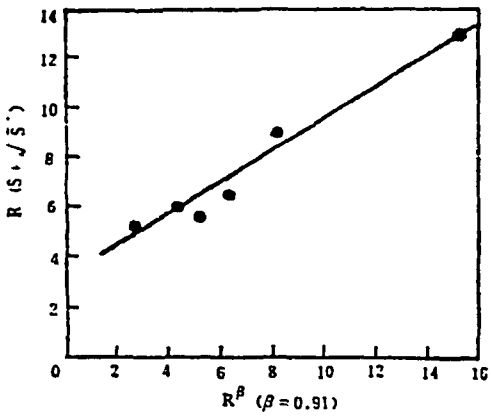


图 2-c 氟-46 的辐照交联(本实验室工作)
Fig. 2-c Radiation crosslinking of F-46 (our laboratory)

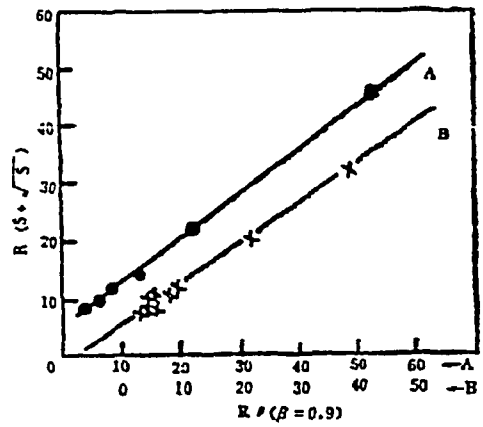


图 2-d PVAc 的辐射交联[11]
Fig. 2-d Radiation crosslinking of PVAc[11]

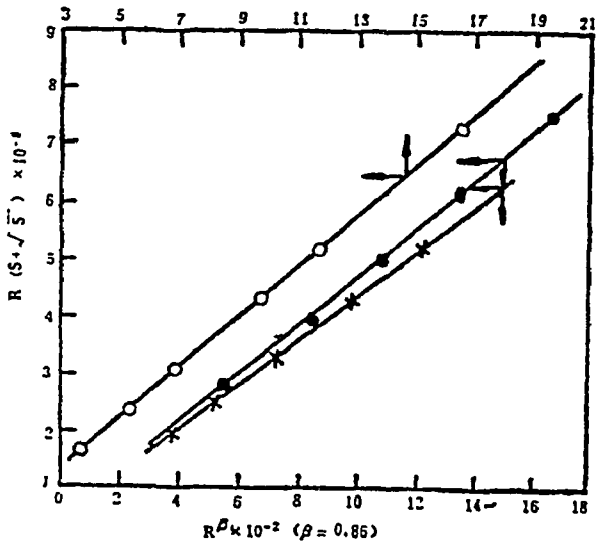


图 3-a PET 的辐射交联[20]
Fig. 3-a Radiation crosslinking of PET[20]
●——N_2 ×——真空 ○——空气

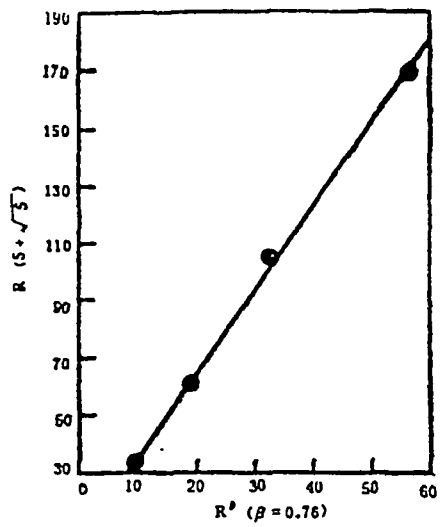


图 3-b 聚丙烯的辐射交联[21](本实验室工作)
Fig. 3-b Radiation crosslinking of polypropylene(our laboratory)

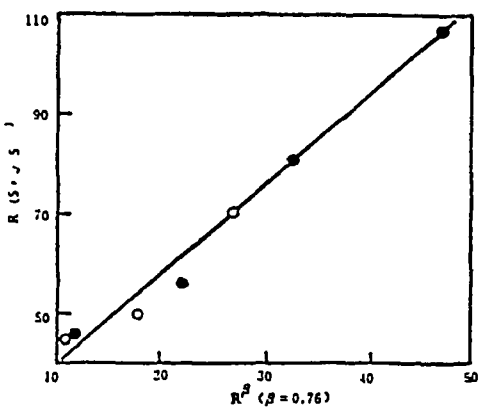


图 3-c 聚丙烯的辐射交联[21]
Fig. 3-c Radiation crosslinking of polypropylene[21]

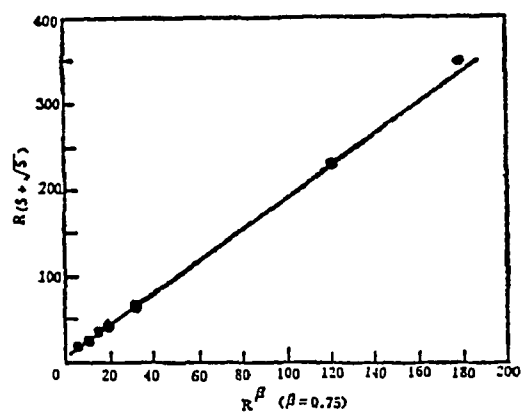


图 3-d 聚己烯的辐射交联[19]
Fig. 3-d Radiation crosslinking of polyhexene[19]

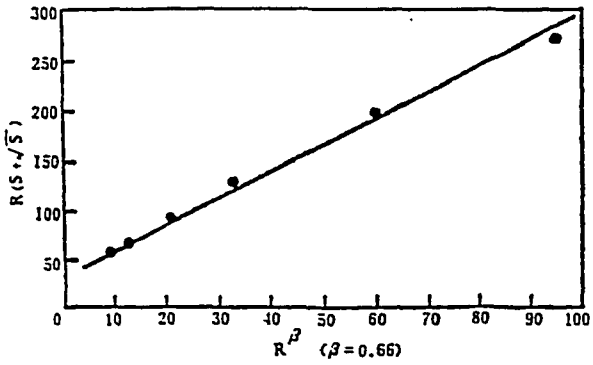


图 3-e 聚戊烯的辐射交联[19]
Fig. 3-e Radiation crosslinking of polypentene[19]

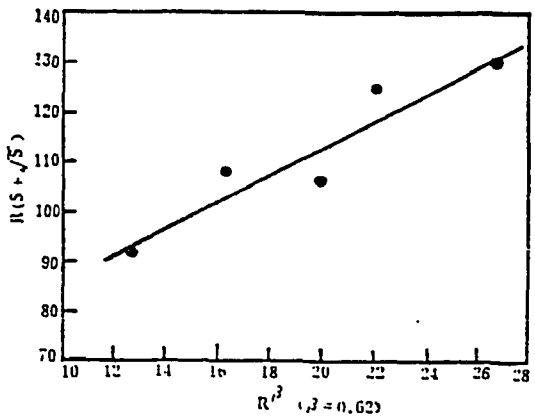


图 4-b 聚氧化乙烯的辐射交联[18]
Fig. 4-b Radiation corsslinking of polyethylene oxide[18]

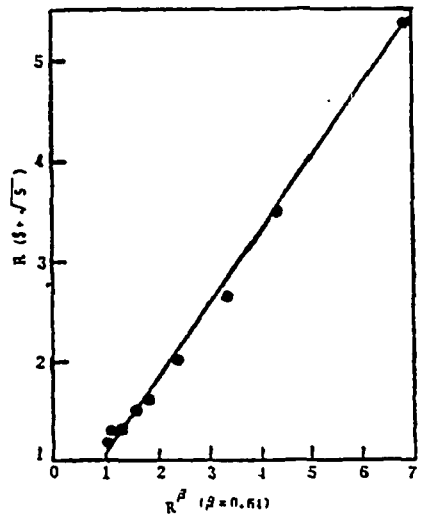


图 4-a 天然橡胶的辐射交联[17]
Fig. 4-a Radiation crosslinking of natural rubber[17]

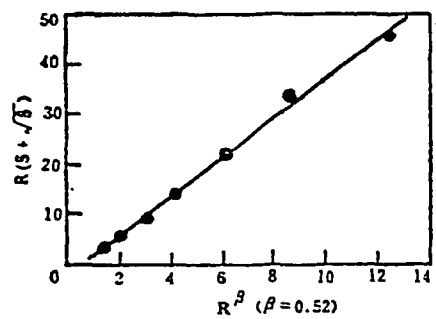


图 4-d 聚乙烯的辐射交联[14]
Fig. 4-d Radiation crosslinking of polyethylene[14]

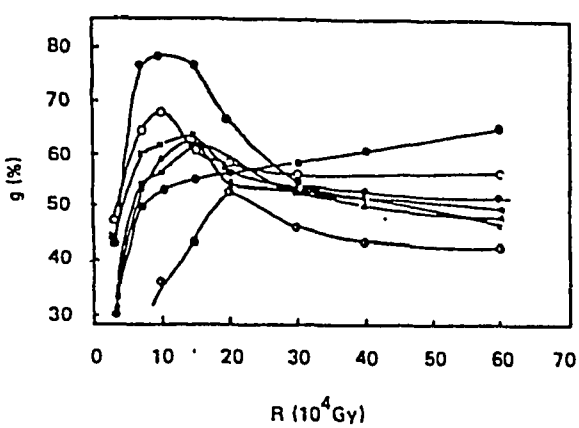
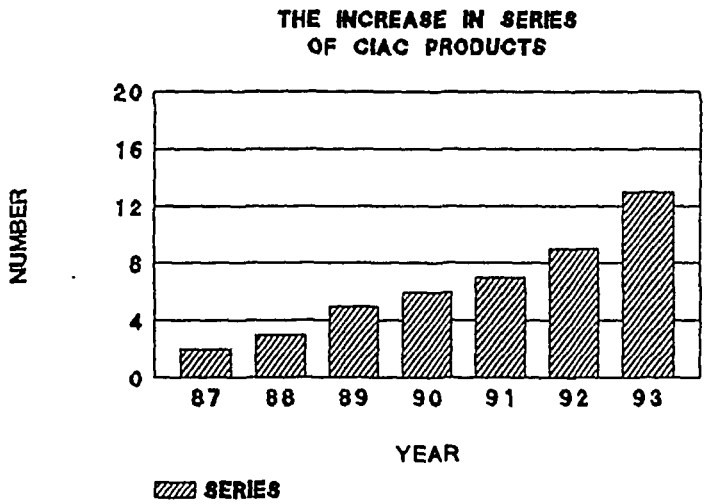
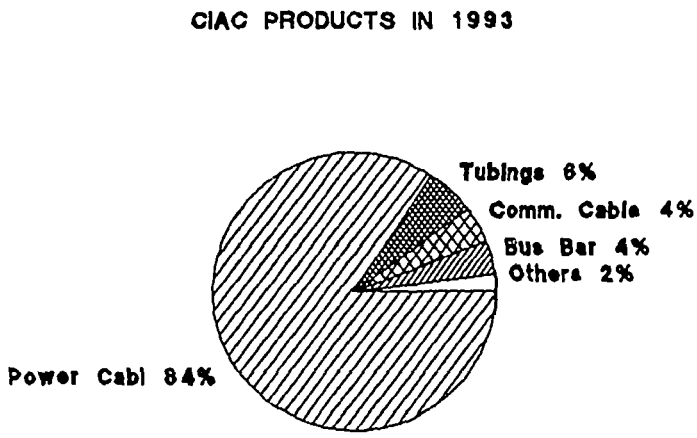


FIG. 1. Relationship between gel content (g) and irradiation dose (R). The content of PMMA: ⊗, 0%; ○, 30%; ●, 70%; ■, 60%; ▲, 50%; X, 40%; ◑, 75%.

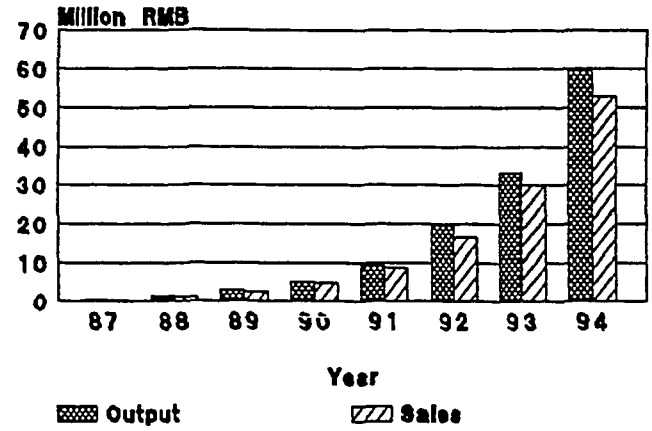
Tab 5. Gel fraction g in melt mixing PIB-EPR blend system obtained under different dose

R(10 kGy)	g(%)	PIB (%)				
		0	50	60	70	80
0	g_B	0	0	0	0	0
4	g_{EPR}	50.1	25	20	15.0	10
	g_{PIB}	0	23	25	19.7	10.1
8	g_{EPR}	71.5	35.8	28.6	21.4	14.3
	g_{PIB}	0	17.7	18.5	25.4	17.1
15	g_{EPR}	82.9	41.4	33.1	24.9	16.6
	g_{PIB}	0	19.4	21.3	30.6	21.1
30	g_{EPR}	87.5	43.7	35.0	26.3	17.5
	g_{PIB}	0	17.9	14.6	32.6	21.3

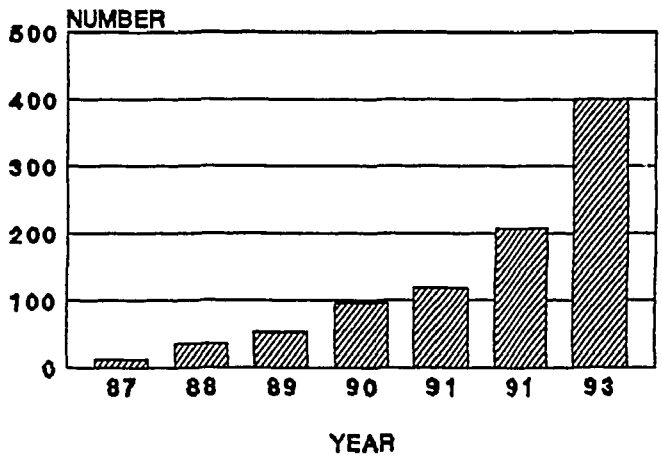




OUTPUT AND SALES OF CIAC PRODUCTS



THE ANNUAL INCREASE IN STAFF



THE INCREASE IN VARIETIES OF CIAC PRODUCTS