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Advanced Research Work on Radiation Cross-linking of Polymers in CIAC

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Abstract

Recent research carried out at the Chinese Institute of Applied Chemistry has contributed significantly to the understanding of the radiation chemistry of polymers. High energy radiation has been successfully used to cross-link fluoropolymers and polyimides. Here chain flexibility has been shown to play an important role, and T-type structures were found to exist in the cross-linked fluoropolymers. A modified Charlesby-Pinner equation, based upon the importance of chain flexibility, was developed to account for the sol-radiation dose relationship in systems of this type. An XPS method has been developed to measure the cross-linking yields in aromatic polymers and fluoropolymers, based upon the dose dependence of the aromatic shake-up peaks and the F/C ratios, respectively. Methods for radiation cross-linking degrading polymers in polymer blends have also been developed, as have methods for improving the radiation resistance of polymers through radiation cross-linking.

The industrial applications of radiation processing of polymers has been growing rapidly in China since the 1980's. The main applications are: the manufacture of radiation cross-linked heat shrinkable materials, radiation cross-linked wire and cable, radiation modified engineering plastics and others. The Changchun Institute of Applied Chemistry (CIAC), as one of the earliest organizations at which fundamental research work on the radiation chemistry of polymers was carried out in China, and it has played a major role in R&D of radiation processing of polymers. Nowadays CIAC owns the largest enterprise involved in the manufacture of radiation cross-linked heat shrinkable materials.

Recent advanced research work on the radiation cross-linking of polymers is summarized below.

1. Radiation cross-linking of fluoropolymers and polyimides.

These studies on the cross-linking of fluoropolymers have included:

(a) The radiation cross-linking of a series of fluoropolymers and copolymers of C_2F_4-C_3F_6 (F-46), C_2F_4-Cl-C_2H_4 (F-40), C_3F_3Cl-C_2H_4(F-30), C_2F_4-$C_2F_3OCF_3$ (F-406), C_2F_4-$C_2F_3OCF_3$-$C_2F_2H_2$ (F-2406), C_2F_6-$C_2F_2H_2$ (F-26), C_2F_6-C_3H_6 (F-60), C_2F_4-C_3F_6-$C_2F_2H_2$ (F-246) and the homopolymers of $C_2F_2H_2$, C_2F_4 and fluoropolyimide (FPI).

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(b) The development of a special solvent for fluoropolymers[1]. We found that fluorochloro oil (an oligomer of C_2F_3Cl) can dissolve many fluoropolymers at high temperature, from which we can get information on the radiation cross-linking of fluoropolymers. Table 1 lists the gel contents of F-30, F-46, and F-406 and Table 2 lists the cross-linking parameters for the fluoropolymers.

(c) Investigations of the property changes in fluorpolymers after cross-linking have also been undertaken. Tables 3, 4 and 5 list respectively the changes in Tm, the rise in the zero strength temperature (ZST) and the improvement in the anti-cracking properties of F-46, which is of great interest in industrial applications. Figure 1 shows the marked improvement in the radiation resistant properties of F-46.

Table 1

Gel content of fluoropolymers

Radiation Dose kGy	F-30	F-46	F-406
0	-	-	-
50	42.4	51	-
100	61.6	68	6 (200 kGy)
500	73.0		40

Table 2

Cross-linking parameters of fluoropolymers

Polymers	F-30	F-46	F-406
Gel Dose / kGy	16	25	178
p_o / q_o	0.3	0.42	1.0
G(X)	1.4	1.16	-

Table 3

The effects of radiation on Tm (°C) of fluoropolymers

Radiation Dose / kGy	FEP	F-30	F-40	PTFE	PVDF
0	257	223	258	334	160
150-300	247	220	244	331	158

Table 4

The ZST of cross-linked fluoropolymers

Radiation Dose kGy	FEP	F-30	PTFE	PFA
0	290	219	390	302
150-300	382	300	420	326

Table 5

The cracking properties of F-46 before and after cross-linking

Testing Method	Gel Content / %	Results
Heat Ageing	0	Cracking after 3 hr
Rolling at 250 °C	51	No cracking after 500 hr
Sheet Stress	0	Cracking after 0.8-2 hr
Cracking	51	No cracking after 48 hr
180 °C in DHN*	58	No cracking after 48 hr

*DHN : Decahydronaphthalene

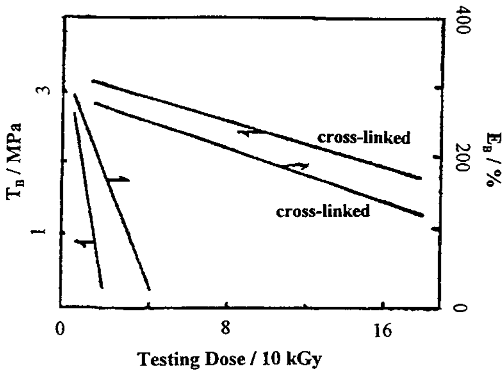


Figure 1. High temperature T_B and E_B for FEP.

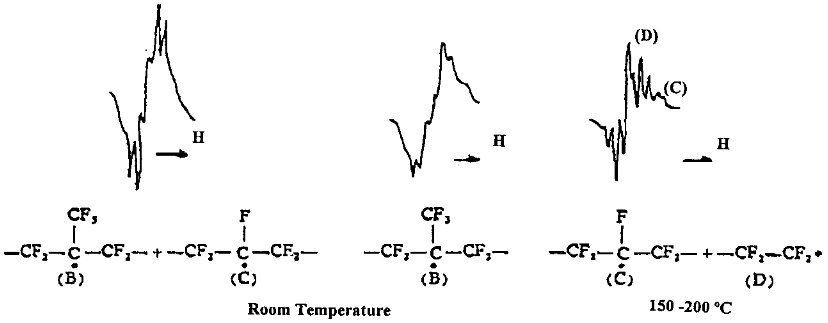


Figure 2. The ESR spectra of fluoropolymer F-46

Table 6

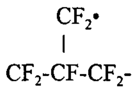
Perfluoropropylene content of F-46

F-46	Perfluoropropylene content / wt%	
	Before irradiation	After irradiation
1	14.9	15.8
2	17.3	18.0
3	19.6	20.9
4	15.7	16.5
5	12.8	13.6

2. *The mechanism of radiation cross-linking of F-46.*

(a) Bowers[2] suggested that the radiation cross-linking of F-46 occurs at the CF_3 side group. The results of our IR spectra[3] show that the CF_3 content is unchanged or slightly rises during irradiation, which means that the CF_3 group is not the main point of cross-linking, as shown in Table 6.

(b) The high temperature ESR spectra, such as at 200°C, show that radical (C) can be detected, but at room temperature radicals (B) (C) and (D) are detected.



$CF_2\text{-}\overset{\overset{CF_2\bullet}{|}}{CF}\text{-}CF_2\text{-}$

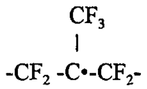
(A)

$\text{-}CF_2\text{-}CF_2\bullet$

(B)

$\text{-}CF_2\text{-}CF\bullet\text{-}CF_2\text{-}$

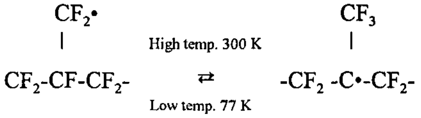
(C)



$\text{-}CF_2\text{-}\overset{\overset{CF_3}{|}}{C}\bullet\text{-}CF_2\text{-}$

(D)

Figure 2. Shows the ESR spectra of irradiated F-46 obtained at different temperatures. Iwasaki[4] interpreted his ESR results in terms of an equilibrium between radicals (A) and (D), as shown below.



$$CF_2\text{-}\overset{\overset{CF_2\bullet}{|}}{CF}\text{-}CF_2\text{-} \underset{\text{Low temp. 77 K}}{\overset{\text{High temp. 300 K}}{\rightleftarrows}} \text{-}CF_2\text{-}\overset{\overset{CF_3}{|}}{C}\bullet\text{-}CF_2\text{-}$$

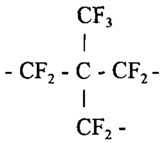
The stability of the of the radicals at high temperature is in the order (C) > (D) > (B) >> (A).

(c) XPS studies on the radiation cross-linking mechanism of F-46 have been carried out[5]. Figure 3 shows the XPS spectra of unirradiated F-46 and F-46 irradiated to a dose of 1100 kGy at 150 °C. Figure 3 shows that after radiation cross-linking two new peaks are observed. One peak P_1 at 289.3 eV was assigned to the CF group in a radiation induced double bond, either:

$$-CF=CF_2 \text{ or } -CF=CF-$$

This observation was proved by IR spectral analysis.

The other peak, P_2, at 287.6 eV belongs to a carbon structure bonded indirectly to an F atom. A possible cross-linked chemical structure is shown below. This structure could result from the combination of radical (D) with radical (B).



$$- CF_2 - \overset{\displaystyle CF_3 \atop |}{\underset{\displaystyle | \atop CF_2 -}{C}} - CF_2 -$$

This means that T type cross-linking occurs in F-46.

The free radical formed in irradiated F-4 at high temperature is very similar to that found in F-46. So we decided toconsider whether F-4 can be crosslinked by irradiation?

3. Radiation Cross-linking of F-4

A lot of workers have reported that the predominant radiation effect on F-4 is degradation. Before 1979 no cross-linking of F-4 had been reported. From our work on radiation cross-linking of F-46, we found that the mechanism of radiation cross-linking of F-46 is T type cross-linking, and the high temperature free radical of irradiated F-4 is very similar to that of F-46. The only difference is in the polymer chain flexibility. The F-4 molecular chain is much more rigid than that of F-46. So , unless the temperature is above its melting point, the bulk viscosity of F-4 is high enough to allow the polymer to maintain its original shape. So F-4 can irradiated at high temperature.

F-4 was irradiated at 330°C-340°C in vacuum and it was found to cross-link[6]. This result was found in 1978 and perfected in 1979, and we were awarded the Chinese national award of invention for this research in 1980. We reported the properties of radiation cross-linked F-4 in 1988 at the IAEA workshop meeting in Hungary[7].

After radiation cross-linking the properties of F-4 are changed. Figures 4-7 show the effects of irradiation temperature and dose on the high temperature tensile strength and elongation of F-4. The figures show that 330°C and 2-20 kGy is the best condition for cross-linking F-4.

TMA curves for F-4 are shown in Fig 8. Curve 3 shows an evident high elastic region beyond the melting point of F-4, which clearly indicates the formation of a cross-linked structure in the irradiated sample. Figure 9 shows the effect of radiation dose on the ZST of F-4 irradiated at

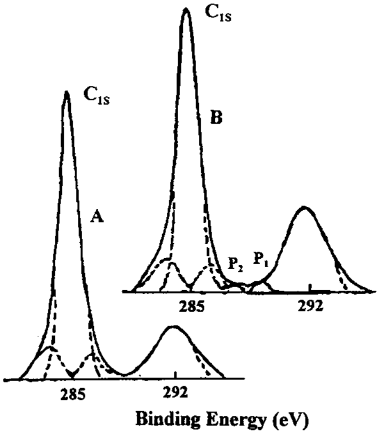


Figure 3. C_{1S} Spectra for FEP. (A) Unirradiated, (B) Irradiated at 150 °C to 1100 kGy.

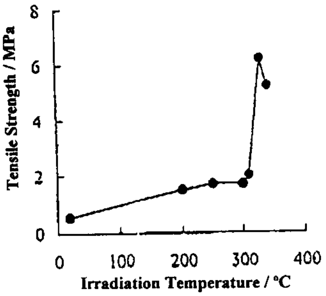


Figure 4. PTFE Tensile Strength at 200 °C (Dose 20 kGy)

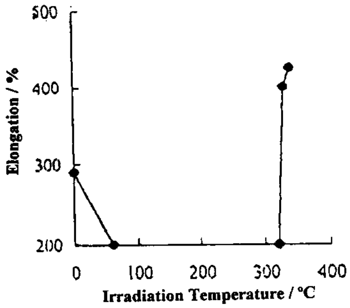


Figure 5. PTFE Elongation at 200 °C. (Dose 20 kGy)

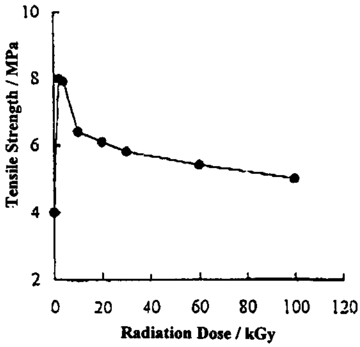


Figure 6. PTFE Tensile Strength versus Dose

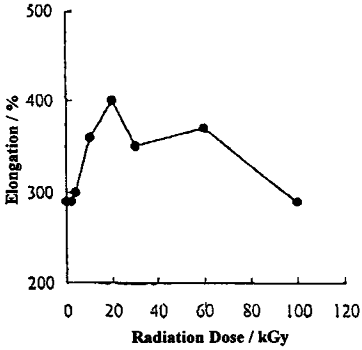


Figure 7. PTFE Elongation versus Dose

ambient temperature and 330°C respectively. After cross-linking, the ZST of F-4 increases gradually in the low dose range which was followed by a gradual decrease above 5 kGy, This is another important fact indicating the formation of a network structure.

The radiation stability of F-4 is also markedly improved after radiation cross-linking. As shown in Figures 10 and 11, the crystallinity and density of F-4 are also different for the degraded and cross-linked polymer.

4. *Radiation Cross-linking of Polyimides.*

Polyimides are well known as engineering plastics because of their high temperature and radiation resistance. But, their high temperature properties with respect to hydrolysis are poor, because the C-N bond is easily hydrolysed. We reasoned that if we used radiation cross-linking technology to produce a radiation cross-linked polyimide, some new -C-C-bond linkages would be produced, and the C-C bond is more stable towards (H_2O) hydrolysis. So the radiation cross-linked polyimide may be stable to water at high temperature.

Table 7

Properties of FPI

Dose / kGy	Gel Content / %	Tg / °C	T_B / MPa	Td / °C
0	0	280	16.7	410
600	8	295	11.3	-
1800	35	310	24.2	430

Table 8

Hydrolysis resistance properties of FPI

Treatment	FPI (Film Control)	FPI (Heat Treatment 10 Days)	FPI (Radiation Cross-linked)
250 °C, H_2O	Powdered	Powdered	Film - Good Tg & E_B Properties
4 MPa, 6 hr	No Strength	No Strength	

Polyimides are also a family of rigid chain polymers, and they are difficult to cross-link by radiation at ambient temperature. However, we found that they can be cross-linked at high temperature[8].

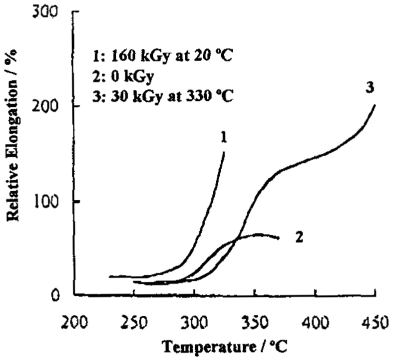


Figure 8. Radiation effect - PTFE TMA curves.

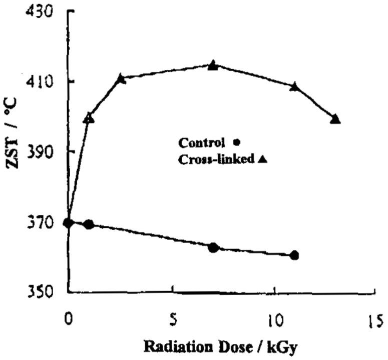


Figure 9. Radiation effect - PTFE ZST.

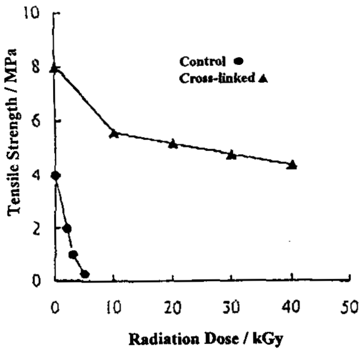


Figure 10. PTFE Tensile strength versus Dose
at 200 °C.

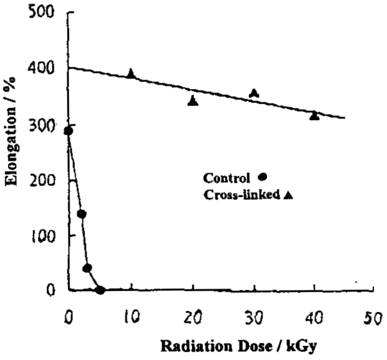


Figure 11. PTFE Elongation versus Dose
at 200 °C.

For fluoropolyimide (FPI) which is irradiated at temperatures much high than Tg, a cross-linked FPI is formed. The properties of cross-linked FPI are shown in Tables 7 and 8.

From this result we can see that the high temperature hydrolysis properties of FPI are markedly improved, which is due to the formation of new C-C bonds after radiation crosslinking. Other polyimides can also be cross-linked by radiation at high temperature, and their high temperature hydrolysis properties are also improved.

It seems that, if the chain flexibility of a rigid chain polymer is changed by heating, fluoropolymers and polyimides can be cross-linked by radiation. So we consider that the flexibility of the chain is the important factor in determining whether irradiation will lead to cross-linking of the polymer.

5. *Modification of the Charlesby-Pinner Equation*

The Charlesby-Pinner Equation[9] is a basic relationship describing the correlation between the sol fraction and the radiation dose. This relationship allows calculation of many important parameters concerning with radiation cross-linking of polymers. The main assumptions associated with Charlesby's equation are:

1. The radiation reaction is random;
2. The molecular weight distribution is in accordance with the Flory distribution;
3. Intramolecular cross-linking is negligible;
4. Chain scission is proportional to radiation dose;
5. Chain cross-linking is proportional to radiation dose.

Based on these assumptions, they obtained the relationship:

$$(S+S^{1/2}) = p_o/q_o + 1/q_o u' \cdot 1/R$$

For some polymer systems, such as those with flexible chains, it was found that the relationship between $(S+S^{1/2})$ and 1/R is not linear as predicted by the equation. Many scientists have suggested that the deviations result from non-Flory molecular weight distributions. However, Chinese scientists Chen-Liu-Tang[10] suggested that for polyethylene, because the polymer chain is very flexible, the equation must be modified, and the density of chain scission will be proportional to the square root of R instead of being proportional to R. They obtained the equation:

$$R\,(S + S^{1/2}) = 1/q_o u' + \alpha_o{}'/q_o \cdot R^{1/2}$$

This equation provided a suitable description of the radiation chemistry for polyethylene.

After the success of this relationship, we reviewed the results of radiation cross-linking of polymers in the literature and found that polymers may be divided into two categories[11]. Table 9 lists the results. From Table 9 we can see that the polymers with higher Tgs obey the Charlesby-Pinner equation because they have a rigid or stiff polymer chain; but polymers with lower Tgs have more flexible polymer chains and they obey Chen-Liu-Tang equation. So, we considered that the chain flexibility of a polymer is the most important factor determining the radiation cross-linking behavior of the polymer.

We proposed that if we associated the chain flexibility with the radiation cross-linking behavior we would be able to obtain a general equation for most polymers. So we introduced a parameter β into the sol-dose equation, and proposed that β is a function of the chain flexibility. We assumed that chain scission is proportional to the radiation dose to the power of β and obtained the equation[12].

$$R(S + S^{1/2}) = 1/q_o u' + \alpha' / q_o R^{\beta}$$

A typical example is that for polypropylene, for which we examined the data obtained in our laboratory. We considered both the Charlesby-Pinner and the Chen-Liu-Tang equations, as well as our general equation, which is shown in shown in Figure 12. A value of β for polypropylene of 0.75 yielded a good linear relationship, but both the Charlesby and Chen equations give a curve.

Table 9

The radiation behaviour of different polymers

Charlesby-Pinner Equation			Chen-Liu-Tang Equation		
Polymer	Tg / °C	Author	Polymer	Tg / °C	Author
Polystyrene	100	Charlesby (1953)	Polyethylene	-125	Alexandeer (1956)
Poly(vinylchloride)	82	Kuriwippler (1960)	Polysilicone (1878) Rubber	-123	Charlesby (1955)
Poly(vinylacetate)	40-45	Charlesby (1969)	Poly(vinylacetate) (Branching)	29-35	Charlesby (1969)
Poly(vinyl alcohol)	85	Ikada	Polypentene	-40	Copper (1959)
Polypropylene		Zhang, Sun (1979)	Polyhexene	-45	Copper (1959)
Polypropylene oxide		Roberts (1971)	Polyester (PET)	69	Hellwege (1963)
F-46	90	Sun (1977)	F-406	10	Qi Zhang (1979)
F-30	50	Luo (1982)	F-2406	-15	Qi Zhang (1979)
F-2 KF-1100		Makuuchi (1976)	F-2 Kynar		Makuuchi (1976)
F-23 KelF3700		Yoshide (1965)	F-26 Viton		Yoshide (1965)

Now we can obtain the Tg of a polymer from the literature or by measurement, and then get a value for β, and use this β value to treat the experimental sol-data. We obtained a linear

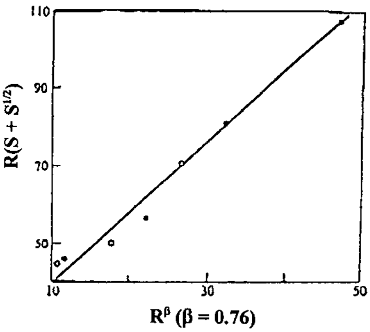


Figure 12. Radiation cross-linking of polypropylene (our work)

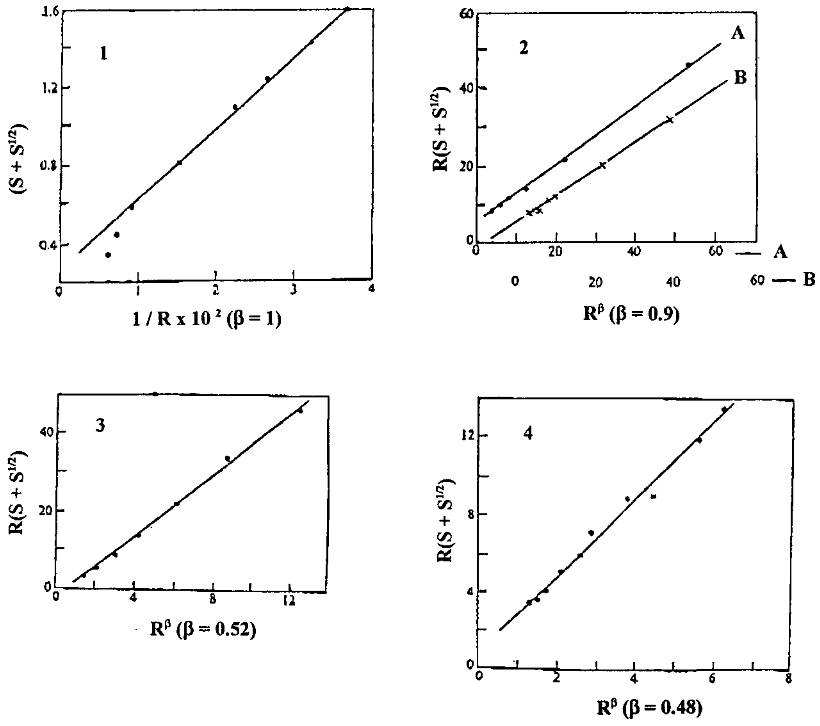


Figure 13. Radiation cross-linking of polymers. (1) Polystyrene
(2) Polyvinylacetate, (3) Polyethylene, (4) polydimethylsiloxane.

relationship for most of polymers. Figure 13 a,b,c,d shows this analysis for the experimental results obtained by different scientists.

We have treated the radiation cross-linking data for a series of fluoropolymers by using the β value. The results are summarize in Table 10[13]. From the table we can see that the chain flexibility of the fluoropolymers is in the following order:

F-2> F-2406 > F-406 > F-30 > F-46 > FPI

The polyimides are a special group of rigid chain polymers for which the β value is >1 and they only undergo cross-linking at high temperature.

Table 10

Values of β for some fluoropolymers

Polymer	Tg / K	$\beta_{exp.}$	$\beta_{cal.}$
F-2	236	0.70	0.68
F-2406	258	0.68	0.72
F-406	283	0.77	0.77
F-30	337	1.0	0.88
F-46	356	0.91	0.92
FPI	546	1.0	1.30

6. *Radiation Cross-linking of Polymer blend Systems.*

Radiation cross-linking of polymer blends is widely used in the manufacture of heat shrinkable materials and the radiation cross-linking of wire and cable industry. Many studies are published as patents. In general, the blends are plastics modified with rubber or rubbers modified with plastic.

We find that the radiation cross-linking behavior of polymer blend systems composed of a radiation degrading type polymer and a radiation cross-linking type polymer are of great interest. Until now, no work has been published in the literature about the radiation cross-linking of radiation degrading polymers without any polyfunctional monomer.

In our laboratory we have found that PMMA can be cross-linked by using the polymer blend technique to produce a cross-linked PMMA without the use of any polyfunctional monomers. We studied a series of PMMAs with other radiation cross-linkable polymers in polymer blend systems. Finally we found that irradiation of PMMA and PEO in a polymer blend can be radiation cross-linked[14] and PMMA enters the gel of the polymer blend system.

Table 11 lists the gel content of PMMA for different compositions and various irradiated doses. It shows that the largest gel content of PMMA is at the region of PMMA/PEO = 70/30 and the most suitable dose is 150 kGy. This is the best condition for radiation cross-linking of the PMMA/PEO polymer blend system. SEM and TEM studies show that this point is in the phase inversion region for the PMMA/PEO polymer blend system.

After radiation cross-linking the properties of the PMMA-PEO blend system are changed. Figure14 shows the TMA scans of the polymer blend system after irradiation. It shows the marked rubber plateau region which exists for the cross-linked polymer blend system, but for the non-cross-linked system of PMMA/PEO = 80/20, no rubber plateau is present, see curve (c).

Table 11

Gel content of PMMA in irradiated PMMA/PEO blend systems

Dose kGy	Percent Gel							
	PMMA %	30	40	50	60	70	75	80
30		26.6	25.9	15.7	19.8	34.6	0	0
70		29.4	29.7	28.0	34.2	62.0	7.0	0
100		30.4	29.3	31.9	34.7	62.1	21.8	0
150		22.0	30.6	34.7	39.6	60.1	34.3	0
200		19.2	22.9	26.0	37.0	50.4	39.2	0
400		-	-	20.1	27.6	34.8	20.9	0
700		10.8	4.9	16.7	22.3	31.3	10.9	0

The behavior of radiation cross-linking of polymer blend systems is uncertain at the phase inversion region, as has already been found in our early work[15]. In the PDMVS/EVA polymer blend system we found some abnormal phenomena. Figure 15 shows the relationship between different parameters and polymer blend compositions. To summarize:

(1) The G-value of cross-linking G(X) and the density of cross-linking value q_o shows a minimum in the phase inversion region.
(2) Dose for gelation Rg changed rapidly in the phase inversion region.
(3) The values of the parameter β in the general equation

$$R(S + S^{1/2}) = 1/q_o\, u' + \alpha_o/q \cdot R^{\beta}$$

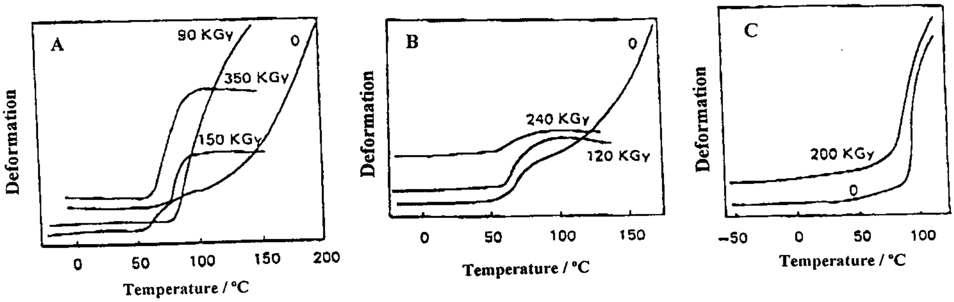


Figure 14. TMA scans on PMMA / PEO.
PMMA / PEO ratios (A) 67/33, (B) 75/25, (C) 80/20.

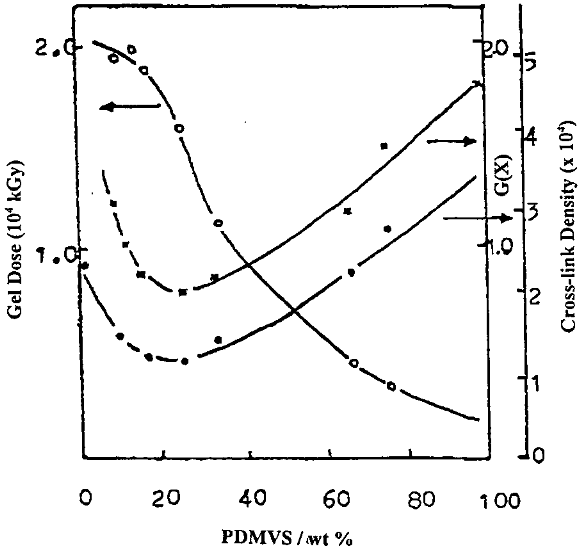


Figure 15. Radiation cross-linking of PDMVS / EVA polymer blend systems.

near the inversion region for polymer blends containing 20, 25, 33 and 55 % PDMVS are $\beta \rightarrow 0.5$, and for blends containing 10,12,16, 66 and 78 %, are $\beta \rightarrow 1$.

This means that at the phase inversion region both of the components are in a continuous phase with no "seas" and no "islands" and the size of the domains of both components are as small as possible. In that condition the components have their largest interfacial areas. This means that the components have much more chance to be in contact with each other.

The question arises; is this cross-linking phenomenon also suitable for other radiation degrading polymers? We selected PIB as another example to examine this question for the five sets of PIB blends with 1,2 PB, PB, EVA, SBR and EPR. We observed cross-linking for the irradiated PIB and EPR blend system in the phase inversion region, with the gel content of PIB listed in Table 12[16].

Table 12

Gel content for radiation cross-linking of PIB/EPR blends

PIB %	Percent Gel			
	40 kGy	80 kGy	150 kGy	300 kGy
50	22	22.7	19.4	17.9
60	24.2	18.5	21.3	14.6
70	19.1	25.4	30.6	32.6
80	9.7	17.1	21.1	21.3

We separated the gel from the polymer blend system, and then carried out a GC-MS analysis. In the gel we detected C-4 species that are characteristic of the presence of PIB. This strongly supports the proposition that PIB has entered the network structure of the polymer blend system.

So, we can conclude that for a blend system containing a radiation degrading type polymer and a radiation cross-linking type polymer, on irradiation a cross-linked structure can be formed in the phase inversion region.

7. *Characterization of Radiation Cross-linking Density of Polymers by the XPS Method*

Because some polymers cannot be dissolved in ordinary solvents, the gel content or cross-linking density cannot be determined by the usual sol-gel method. We therefore tried to find some new methods to determine the cross-linking density. One of them is the XPS method. We used this method for the first time to determine the cross-linking density for fluoropolymers and for polymers containing a phenyl ring.

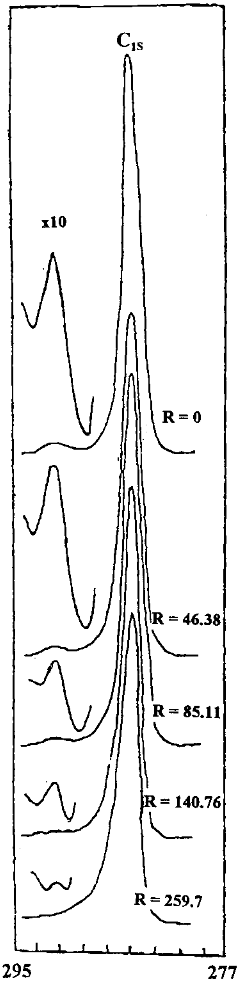


Figure 16. ESCA spectrum of polystyrene at different doses (Mrad).

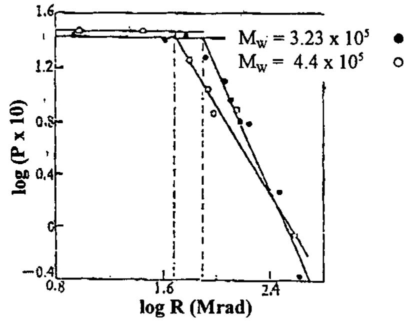


Figure 17. The log P versus log R for polystyrene.

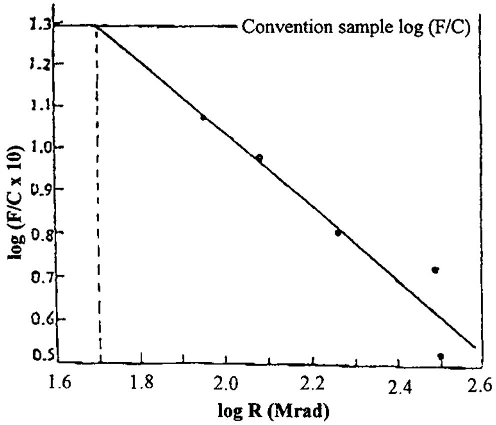


Figure 18. Log (F/C) versus log R for FPI.

A. Phenyl ring containing polymers.

Clark has pointed out that the shake-up peak is characteristic of the π-electron conjugated system of phenyl ring containing polymers. So we have studied the change in the shake-up peaks of some phenyl ring-containing polymers before and after γ-irradiation or radiation cross-linking.

Zhang W.X. et al.[17] studied the XPS spectrum for the radiation cross-linking of polystyrene, and found that the shake-up peak of polystyrene is decreased with increasing radiation dose, as shown in Figure 16. This means that the conjugated system is decreased with increasing radiation cross-linking density.

A plot of log Ps (where Ps is the area ratio of the shake-up peak to the main peak) against log R (the radiation dose) consists of two straight lines which have an intersection point which corresponds to the gel dose. This value of the gelation dose is very close to the value found by the gel-sol method as shown in Fig 17 and Table 13.

Table 13

The gel dose and G(X) for radiation cross-linking of polystyrene.

Molecular Weight g mol^{-1}	Gel Content Method		XPS Method	
	Gel Dose	G(X)	Gel Dose	G(X)
3.23 x 10^5	79	0.019	79.4	0.019
4.4 x 10^5	52	0.021	50.1	0.022

Zhong X.G. et al. [18] studied the radiation cross-linking of polysulfone by the XPS method. We found that when irradiated at room temperature, the shake-up peak area decreased with increasing radiation dose. The behaviour is similar to that observed in the case of polystyrene. But when polysulfone was irradiated at high temperature, the intensity of the shake-up peak of polysulfone increased with increasing of radiation dose. The plot of log Ps against log R consists of two straight lines, and from the intersection we can find the gelation dose. Table 14 lists the results which show that the R-gel value from the XPS and sol-gel methods are in very close agreement.

Table 14

The gelation dose for polysulfone

Irradiation Temperature °C	Gel Dose / kGy (XPS Mehod)	Gel Dose / kGy (Gel Content Method)
203	270	279
174	395	389

B. Fluoropolymers[19]

Some fluoropolymers have no solvent, so the cross-linking density cannot be determined by the gel content method. We have examined the use of the XPS method to determine the cross-linking density of fluoropolymers, and to solve the problem of characterization of the cross-linking degree for insoluble fluoropolymers. First we examined F-46 and FPI. Generally, in radiation cross-linking of fluoropolymers, defluorination and dehydrofluorination reactions occur, which lead to a decrease in the amount of fluorine present, so also a decrease in the ratio of F/C.

(a) The radiation crosslinking of F-46

F-46 is a polymer of the perfluoro-type, and the cross-linking occurs through defluorination and this gives rise to a decrease in the ratio of fluorine to carbon (F/C) with increasing cross-link density. Table 15 lists XPS measurements obtained from a log (F/C) vs log R plot from which we can find the gelation dose from the intersect of the two straight lines.

Table 15

Gel dose values for F-46

Irradiation Temperature °C	Gel Dose / kGy (XPS Method)	Gel Dose / kGy (Sol-gel Method)
240	17.4	20.0

(b) The radiation cross-linking of FPI

After radiation cross-linking, the area of the peak at a binding energy of 293 eV shows a decrease that is associated with the CF_3 group. When radiation cross-linking occurs the XPS spectrum shows that the area of the peak attributed to the CF_3 group (binding energy of 293 eV) decreases with increasing cross-linking density. Figure 18 shows the decreasing (F/C) ratio with increasing radiation dose (R). The gel doses obtained by the XPS and sol-gel methods and the results are in very close agreement: XPS method R-gel = 500 kGy, sol-gel method R-gel = 570 kGy.

(c) Radiation Cross-linking of F-40[20]

F-40 is considered to be an insoluble polymer, so its cross-linking density cannot be determined by the gel content method. During radiation cross-linking the F/C ratio decreases with increasing radiation dose. Figure 19 shows the relationship between F/C and R, and from the intersection of the two straight lines, a dose for gelation of about 41 kGy is obtained.

8. Improvement of Radiation Resistance Properties by Crosslinking to Form a Network Structure.

The mechanical properties of polymers strongly depend on their molecular weight. Thus polymers

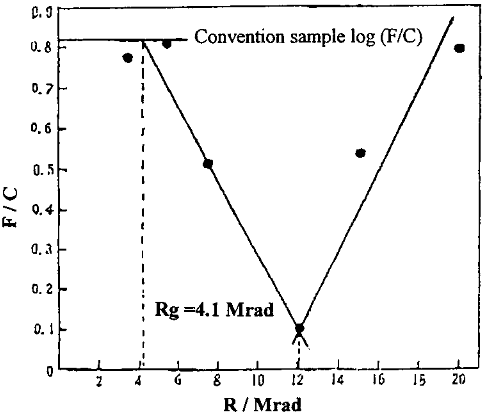


Figure 19. The relationship between F/C and Dose for F-40.

with higher molecular weight generally show better mechanical properties relative to polymers with lower molecular weight. In actual applications, a commonly used method for preventing a polymer from molecular chain fracture caused by aging is to incorporate an antioxidant. In the case of exposure to ionizing radiation, however, besides cross-linking, some polymers will predominantly undergo a reduction of molecular weight. For these polymers, the molecular structure makes their molecular chain very sensitive to radiation and even small radiation doses lead their molecular chain to fracture and thus they then have poor mechanical properties. However, for radiation cross-linkable polymers the molecular weight increases with increasing radiation dose, and thus their mechanical properties are improved markedly, and these polymers can also be called radiation resistant polymers. The main purpose of the present work was to examine the conditions for crosslinking.

(a) The radiation behaviour of F-46

The data in Table 16 indicate that for linear F-46, when irradiated in air at room temperature, degradation clearly occurs and for irradiations up to 20 kGy the polymer shows no elongation. But for cross-linked F-46, the radiation stability shown by the changes in mechanical properties have improved markedly.

Table 16

Properties of F-46 before and after radiation aging

Aging Dose kGy	Linear F-46		Cross-linked F-6	
	*TB / MPa	*EB / %	*TB / MPa	*EB / %
0	3.3	350	4.0	300
5	3.0	225	-	-
10	2.5	105	-	-
20	1.7	0	2.8	270
30	1.0	0	-	-
40	-	-	2.6	250
80	-	-	2.3	200
100	-	-	2.2	180
150	-	-	1.7	110

The conditions for radiation cross-linking are: 240°C, vacuum, 100 kGy.
*TB: Tensile Strength, EB: Elongation and Test temperature: 200°C

(b) The radiation behaviour of F-4

The improvement in the radiation resistance is similar to that of F-46 shown in Figure 10.

(c) The polymer blend system PMMA/PEO is a typical radiation degrading polymer and low dose irradiations cause the mechanical properties decrease quickly. Table 17 lists the change in the mechanical properties of the system for various blend compositions under different radiation treatments. A reasonable explanation for this phenomenon is that radiation cross-linking occurs and the network structure protects against or delays the degradation reaction.

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