

## Improvement of Adhesive Properties of Plastics by Radiation Graft Polymerization

KAZUO MANAKA and TAMOTSU TOMIOKA, *Tokyo Shibaura Electric Company, Central Research Laboratory, Kawasaki, Japan*

### Synopsis

Epoxy compounds such as allyl glycidyl ether, phenyl glycidyl ether, and Epicote 812, which are not polymerizable by irradiation, were irradiated by  $\gamma$ -rays to a total dose of  $1 \times 10^7$ – $2 \times 10^8$ r, and decomposition of epoxy radicals was examined. The result showed that epoxy radicals are more or less radiation-resistant and for the greater part remain unchanged. Methacryl glycidyl ester, which is polymerizable by irradiation, was radiation-grafted to polyethylene and to polytetrafluoroethylene by simultaneous irradiation with  $\gamma$ -rays, and the degree of grafting was checked. Two sheets of radiation-graft polyethylene or polytetrafluoroethylene were bonded with epoxy resin adhesives containing polyamide hardener, and bond strength was examined. This showed that the bond strength of grafted polymer is larger than that of the non-grafted one.

### INTRODUCTION

Polyethylene and polytetrafluoroethylene are plastics known to have very poor adhesive properties. To improve the adhesive properties of polyethylene, surface treatments with chemical reagents,<sup>1</sup> electrical discharges,<sup>2</sup> flames,<sup>3</sup> or ionic radiation<sup>4</sup> have been generally performed for the purpose of oxidizing its surfaces. In the case of polytetrafluoroethylene, surface treatment with sodium-naphthalene complex<sup>5</sup> has been performed to make its surface polar.

Recently, Rieke and Hart<sup>6</sup> reported that they tried to graft acrylic acid to polyethylene by radiation graft polymerization and as a result they could improve its adhesive properties.

In the present study, we report on an attempt to graft methacryl glycidyl ester to polyethylene and to polytetrafluoroethylene by radiation graft polymerization to improve adhesive properties.

### EFFECT OF IONIC RADIATION ON EPOXY COMPOUNDS

In radiation graft polymerization of methacryl glycidyl ester (MGE) to polyethylene and to polytetrafluoroethylene, it is necessary first to examine how much damage to the epoxide rings is produced by radiation. We therefore first investigated this respect by using model epoxy com-

pounds such as allyl glycidyl ether (AGE), phenyl glycidyl ether (PGE) and Epicote 812 (Shell Chemical Co.), irradiating such compounds by  $\gamma$ -rays in air or in vacuum and determining the decrease of epoxy radicals content.

### Experimental

We used AGE and PGE which were distilled repeatedly under reduced pressure. In the case of Epicote 812, the commercial product was used without any further treatment. These compounds were irradiated with  $\gamma$ -rays from a 800-curie  $\text{Co}^{60}$  source at a dose rate of  $2 \times 10^5$  r/hr.

For the irradiations in air, these compounds were put into open glass tubes and irradiated. For the irradiation in vacuum, the compounds were degassed by repeated freezing and melting by the use of liquid nitrogen, placed in ampules which were then sealed and irradiated.

For the quantitative determination of double bonds, we used the potassium tribromide method.<sup>7</sup> In this method, after dissolving bromine in an aqueous solution of potassium bromide and standardizing this tribromide solution with potassium iodide and sodium thiosulfate, we added this solution to the samples and titrated excess reagent by potassium iodide.

For the quantitative determination of epoxy radicals, we used the hydrogen chloride-dioxane solution method,<sup>8</sup> in which a solution of concentrated hydrochloric acid in dioxane is added to the samples and excess hydrochloric acid titrated by standardized sodium hydroxide.

We also measured infrared absorption spectra of irradiated or nonirradiated epoxy compounds.

### Results

**Decrease of Double Bonds.** The results of irradiation of AGE in air or in vacuum are shown in Table I. The value  $\text{Br}/W$  appearing in the table is the ratio of bromine (Br) consumed in titration to the weight  $W$  of samples; i.e., the value of  $\text{Br}/W$  is a measure of the double bond content.

Table I shows that the decrease of double bonds is much larger in air than in vacuum. This may be due to the oxidation by air.

TABLE I  
Decrease of Double Bonds in AGE Irradiated in Air or in Vacuum

Irradiation atmosphere	Total dose, r	$\text{Br}/W$
Air	0	1.40
	$1 \times 10^7$	0.98
	$2 \times 10^8$	0.75
Vacuum	0	1.40
	$5.5 \times 10^6$	1.30
	$8.2 \times 10^7$	1.13

TABLE II  
Decrease of Epoxy Radicals in AGE Irradiated in Air or in Vacuum

Irradiation atmosphere	Total dose, r	Epoxy value
Air	0	0.88
	$1 \times 10^7$	0.83
	$2 \times 10^8$	0.64
Vacuum	0	0.88
	$5.5 \times 10^6$	0.70
	$1.3 \times 10^8$	0.65

**Decrease of Epoxy Radicals.** The results of irradiation of AGE in air or in vacuum are shown in Table II. The epoxy values decrease gradually on irradiation but there is almost no difference between the values in air and in vacuum.

The results of irradiation of PGE in vacuum are shown in Table III.

TABLE III  
Decrease of Epoxy Radicals in PGE Irradiated in Vacuum

Total dose, r	Epoxy value
0	0.67
$1 \times 10^7$	0.67
$2 \times 10^8$	0.63

There is almost no decrease in epoxy values of PGE. This is certainly due to the protective effect of benzene rings against irradiation.

The results of irradiation of Epicote 812 in air are shown in Table IV.

TABLE IV  
Decrease of Epoxy Radicals in Epicote 812 Irradiated in Air

Total dose, r	Epoxy value
0	0.67
$1 \times 10^7$	0.64
$2 \times 10^8$	0.40

Table IV shows the decrease in epoxy values, but many epoxy radicals may still remain with an irradiation dose of  $1 \times 10^7$ – $1 \times 10^8$  r.

**Infrared Absorption Spectra.** The infrared absorption spectrum of AGE irradiated in vacuum clearly shows the formation of —OH radicals and =CO radicals (Fig. 1), but the decrease of double bonds and epoxy radicals can not necessarily be recognized. On the other hand, the spectrum of AGE which was irradiated in air, definitely shows formation of

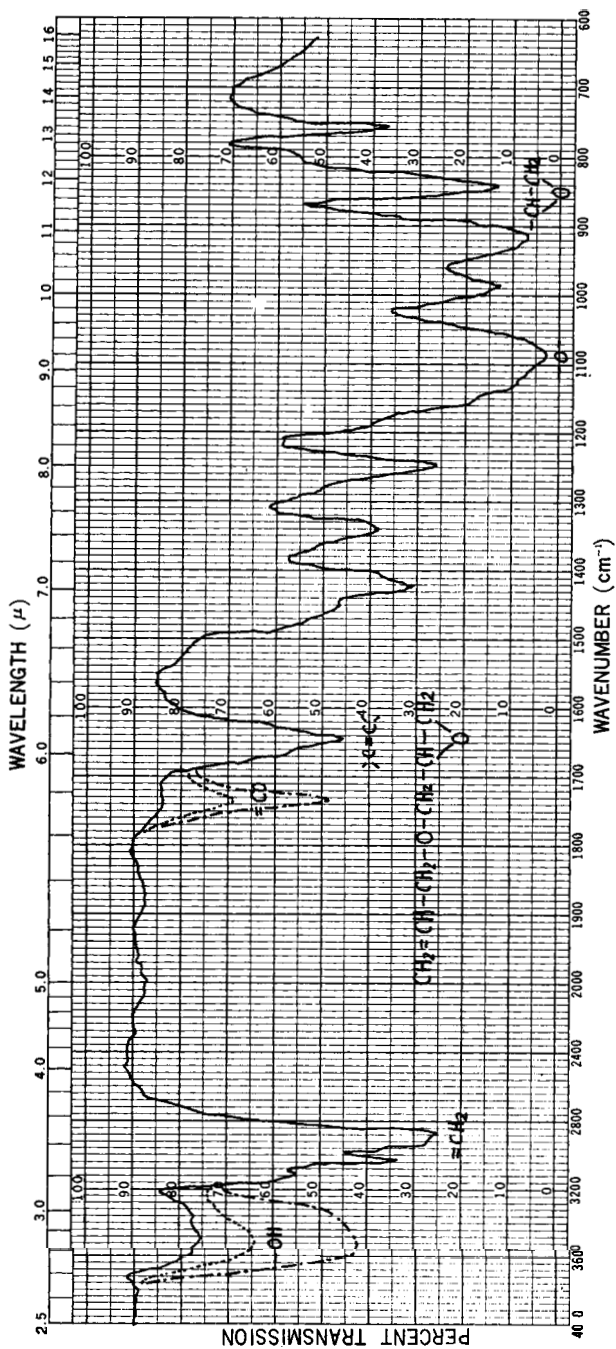


Fig. 1. Irradiation of AGE: (— · —) in air; (---) in vacuum; (—) no treatment.

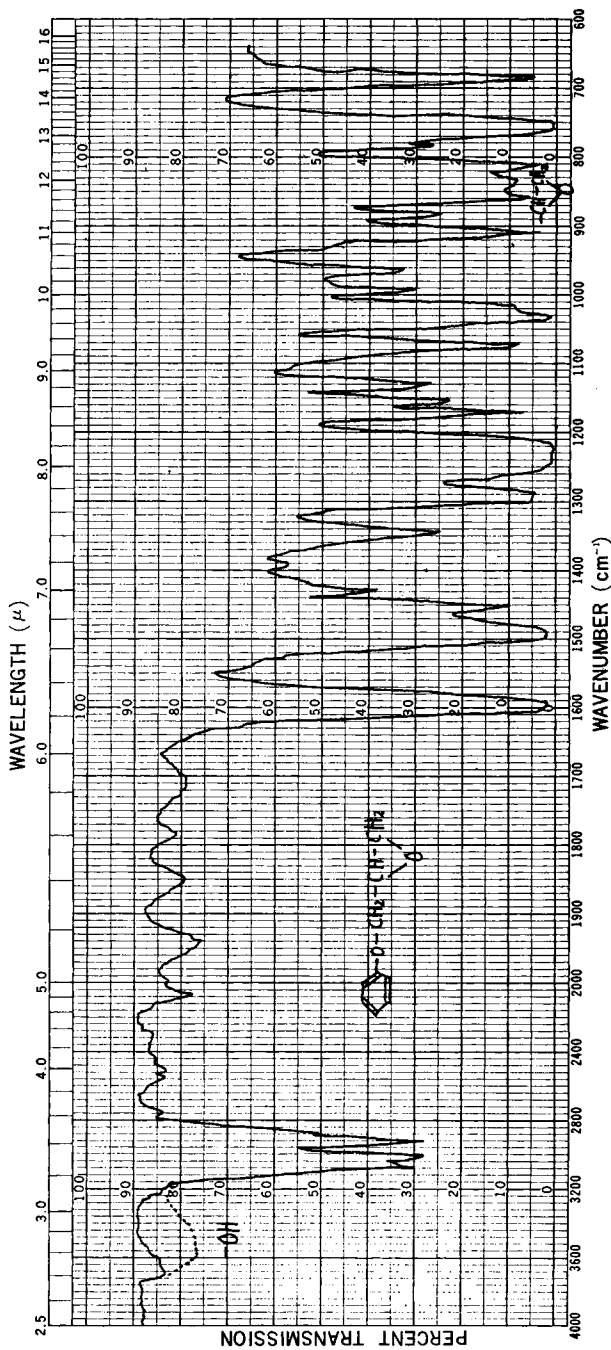


Fig. 2. Irradiation of PGE: (---) in vacuum; (—) no treatment.

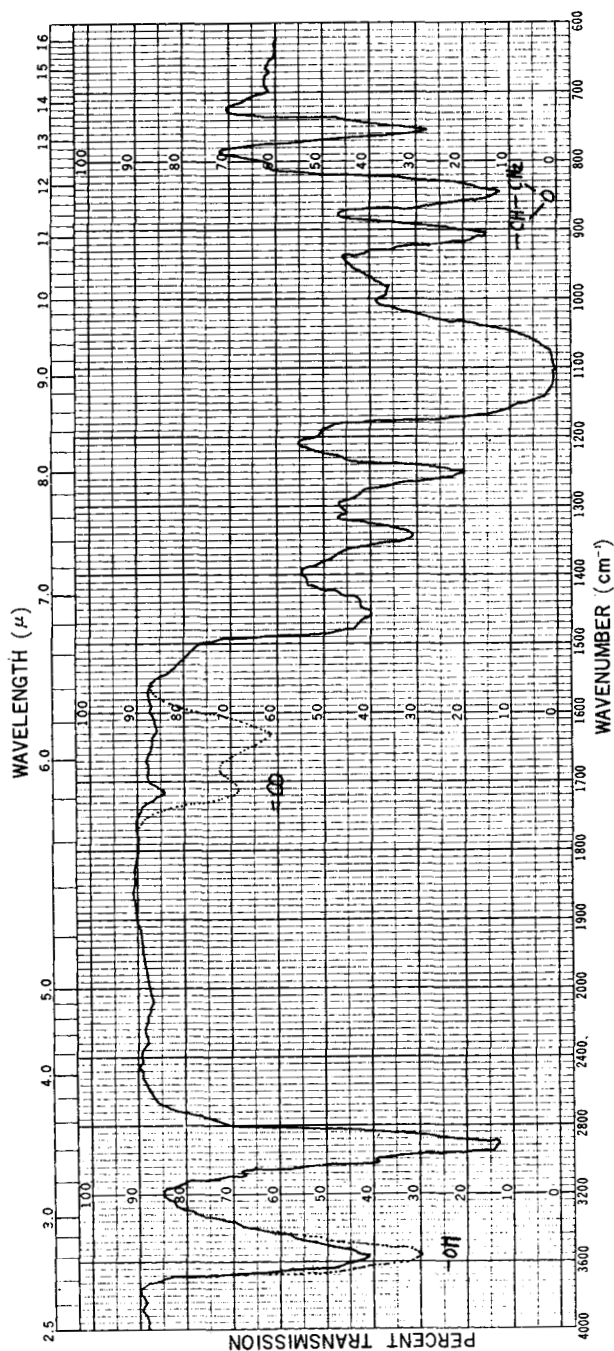


Fig. 3. Irradiation of Epicote 812: (---) in air; (—) no treatment.

—OH and =CO radicals as (Fig. 1), and there are some indications of a decrease in double bonds and epoxy radicals, although they are not clear.

The absorption spectrum of PGE which was irradiated in vacuum shows only the slight formation of —OH radicals as in (Fig. 2), and the absorption spectrum of Epicote 812 which was irradiated in air shows clearly the formation of —OH and =CO radicals (Fig. 3).

### RADIATION GRAFT POLYMERIZATION OF METHACRYL GLYCIDYL ESTER TO POLYETHYLENE AND POLYTETRAFLUOROETHYLENE

From the above experiments, we recognized that the epoxy radicals are not necessarily weak to irradiation and their greater position still remains unchanged after an irradiation dose  $1 \times 10^7$  r. Therefore, we concluded that when an epoxy compound is used as monomer in radiation graft polymerization, the grafted epoxy compound may have considerable epoxy radical content.

AGE does not polymerize either by radiation or by catalysis, nor does it not graft to any polymers. We therefore used methacryl glycidyl ester (MGE) in grafting, as this monomer can easily polymerize or graft to many polymers.

#### Experimental

We grafted MGE by simultaneous irradiation of on 0.05 mm. films of polyethylene and polytetrafluoroethylene. The polyethylene used was a low-density polymer having a density of 0.92, and the polytetrafluoroethylene was a commercial product of E. I. du Pont de Nemours & Co. We washed these films in benzene and in methanol repeatedly. MGE was distilled under reduced pressure and diluted with proper solvents.

The polymer films and MGE solutions were put into glass tubes and degasses by repeat freezing and melting with liquid nitrogen under evacuation to  $10^{-3}$  mm. Hg. The glass tubes were then sealed and irradiated at a dose rate of  $2 \times 10^1$  r/hr. with  $\gamma$ -rays from a  $\text{Co}^{60}$  source.

#### Results

**Grafting to Polyethylene.** Grafting, carried out with benzene as the solvent, yielded the results shown in Table V.

The infrared absorption spectrum of the film obtained in experiment 5 in Table V, shows clearly the presence of MGE grafted to polyethylene (Fig. 4).

When we used dimethylformamide (DMF) as the solvent, the results of Table VI were obtained.

When tetrahydrofuran (THF) was used as the solvent, the results of Table VII were obtained.

When we compared the results of Tables V–VII, we found that the order of degree of grafting is as follows: benzene > THF > DMF.

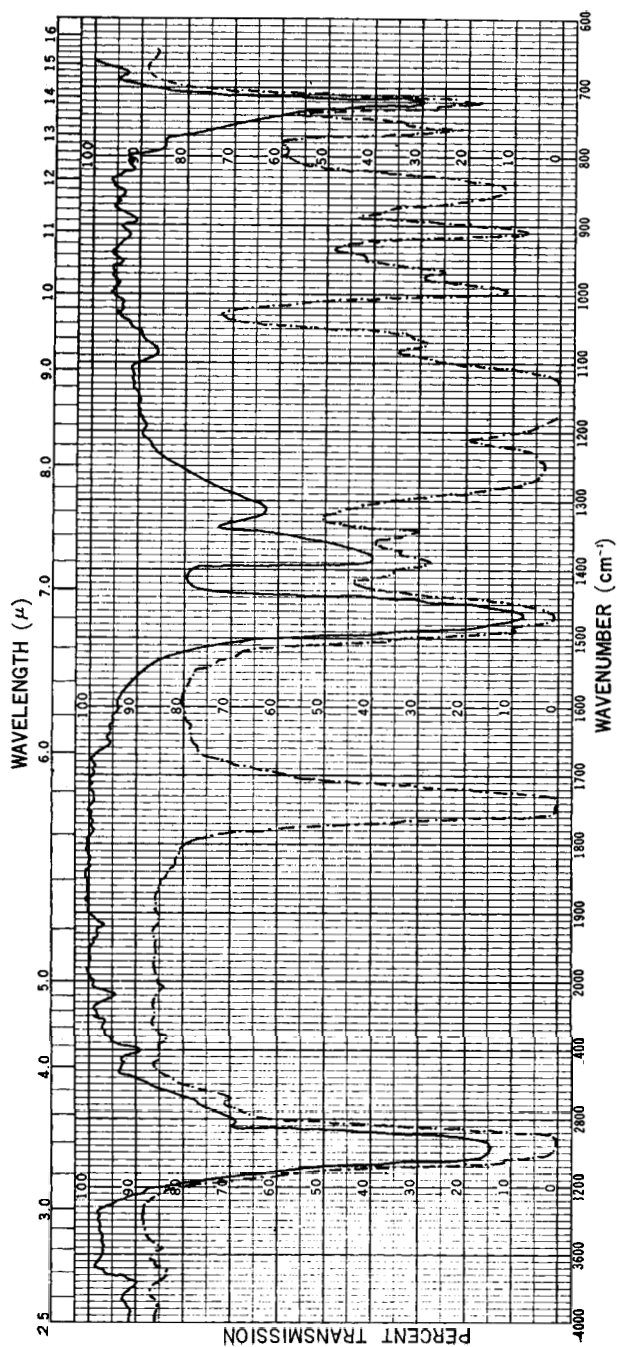


Fig. 4. Grafting of MGE to polyethylene: (---) graft copolymer; (—) polyethylene.



TABLE V  
Grafting to Polyethylene with Benzene as Solvent<sup>a</sup>

Expt. no.	Concentration of solutions, %	Degree of grafting, %	Remarks
1	80	—	Contents all solidified
2	50	—	
3	20	—	Film swelled to four-fold area
4	10	—	Film swelled markedly
5	5	85	Film extracted with THF

<sup>a</sup> Total dose:  $1 \times 10^7$  r.

TABLE VI  
Grafting to Polyethylene with DMF as Solvent<sup>a</sup>

Expt. no.	Concentration of solutions, %	Degree of grafting, %	Remarks
1	50	—	Contents all solidified
2	40	—	
3	30	167	
4	20	100	Extracted with THF
5	10	60	

<sup>a</sup> Total dose:  $1 \times 10^7$  r.

TABLE VII  
Grafting to Polyethylene with THF as Solvent

Expt. no.	Concentration of solutions, %	Degree of grafting, %	Remarks
1	10	78	Grafted films are flat and smooth
2	5	13	

<sup>a</sup> Total dose:  $1 \times 10^7$  r.

Benzene is a good solvent from the point of view of degree of grafting, but it is disadvantageous in respect to the appearance, that is, the surfaces of the grafted films are wavy. In consequence, THF is the solvent of choice with respect to both the degree of grafting and for the appearance of grafted films.

**Bond Strength of Grafted Polyethylene.** Specimens of polyethylene for testing bond strength, having the dimensions  $1 \times 10 \times 40$  mm., were grafted by the method described above by using MGE as a 5% solution in THF, irradiating to a total dose of  $1 \times 10^7$  r, and extracting repeatedly with THF.

Two pieces of grafted specimen were overlapped on both ends to an area of  $1 \text{ cm.}^2$ , the area being coated beforehand with adhesives consisting of epoxy resin and polyamide resin containing 10% resorcinol as promotor. The pieces were joined with paper clips for 2 days at room temperature and

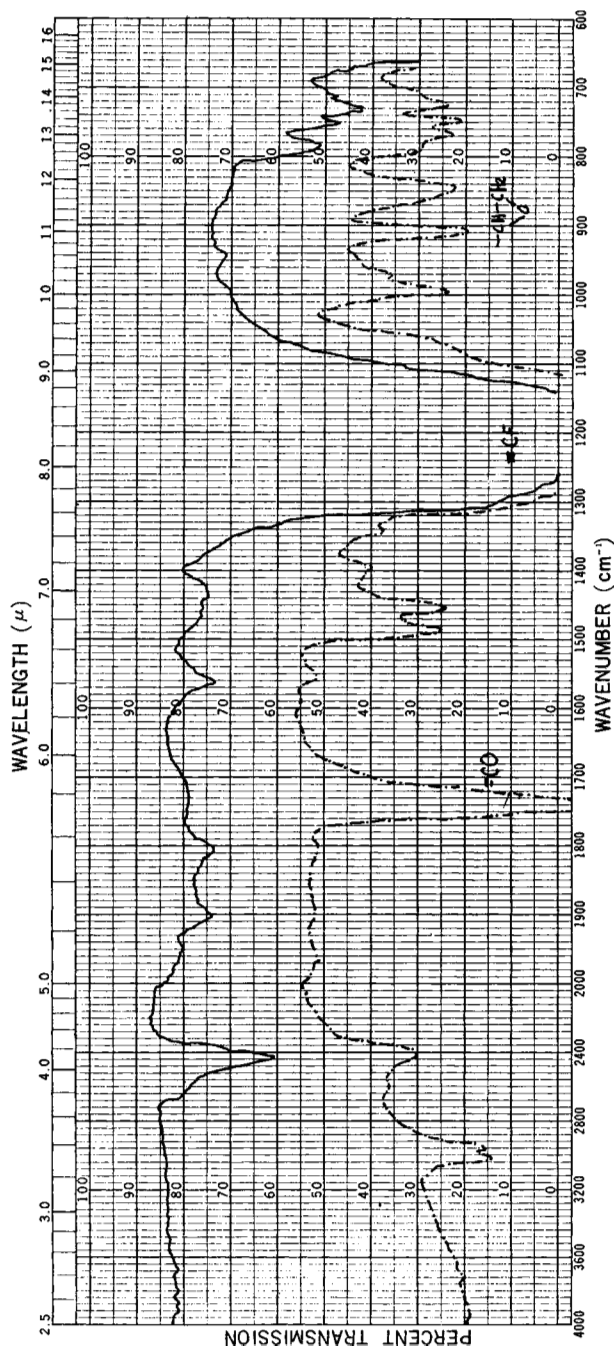


Fig. 5. Grafting of MGE to polytetrafluoroethylene: (- · -) graft copolymer; (—) polytetrafluoroethylene.

bond strengths then tested at a pulling speed of 5 mm./min. using a tensile testing instrument.

The average shear strength was found to be 13 kg., while the shear strength of nongrafted specimens bonded with the same adhesives had a strength of only 2 kg. For reference, we tested the shear strength of the test piece itself and found that it was 15 kg., i.e., 2 kg. larger than the bond strength.

**Grafting to Polytetrafluoroethylene.** We irradiated to a total dose of  $1 \times 10^7$  r with benzene as the solvent, and the results of Table VIII were obtained.

TABLE VIII  
Grafting to Polytetrafluoroethylene with Benzene as Solvent<sup>a</sup>

Expt. no.	Concentration of solutions, %	Degree of grafting, %	Remarks
1	80	—	Contents all solidified
2	50	—	
3	20	—	Film became hard and wavy
4	5	26	Extracted with THF

<sup>a</sup> Total dose:  $1 \times 10^7$ r.

With PMF as the solvent, we obtained the results of Table IX.

TABLE IX  
Grafting to Polytetrafluoroethylene with DMF as Solvent<sup>a</sup>

Expt. no.	Concentration of solutions, %	Degree of grafting, %	Remarks
1	50	—	Contents all solidified
2	40	—	
3	30	7	
4	20	3	
5	10	1	
6	5	0.2	

<sup>a</sup> Total dose:  $1 \times 10^7$ r.

With THF as the solvent, we obtained the results shown in Table X.

TABLE X  
Grafting to Polytetrafluoroethylene with THF as Solvent<sup>a</sup>

Expt. no.	Concentration of solutions, %	Degree of grafting, %	Remarks
1	30	31	
2	20	36	Grafted films are flat and smooth
3	10	14	
4	5	2	

<sup>a</sup> Total dose:  $1 \times 10^7$ r.

The infrared absorption spectrum of the film obtained by experiment 3 in Table X shows the presence of MGE grafted to polytetrafluoroethylene (Fig. 5).

Owing to the poor radiation resistance of polytetrafluoroethylene, the films grafted at  $1 \times 10^7$ r were generally so fragile that they seemed not usable practically. Then, we decided to irradiate total dose of  $1 \times 10^6$ r in grafting.

Using THF as a solvent and total dose of  $1 \times 10^6$ r, we obtained the results of Table XI.

TABLE XI  
Grafting to Polytetrafluoroethylene<sup>a</sup>

Expt. no.	Concentration of solutions, %	Degree of grafting, %	Remarks
1	50	19	
2	40	21	
3	30	17	Grafted films are flat and smooth
4	20	4	
5	10	1	
6	5	0	

<sup>a</sup> Solvent: THF, total dose:  $1 \times 10^6$ r.

From the above experiments, we concluded that THF is the best solvent.

**Bond Strength of Grafted Polytetrafluoroethylene.** We determined the bond strength of grafted polytetrafluoroethylene by a method similar to that used in case of polyethylene. Test specimens,  $1 \times 10 \times 40$  mm., were grafted with a 30% solution MGE in THF under total irradiation dose  $1 \times 10^6$ r. Two grafted specimens were bonded as before, and shear strength tested in the same way as with polyethylene.

The average shear strength was found to be 14 kg., and failure occurred in specimens themselves, while the nongrafted specimens showed a shear strength of 1.5 kg. For reference, the shear strength of a nongrafted specimen itself was tested and found to be 19 kg., so that it became clear that polytetrafluoroethylene itself decreased its strength even at a dose of  $1 \times 10^6$ r.

## DISCUSSION

The radiation resistance of epoxy radicals in epoxy compounds was thought to be very small and the radicals easily decomposed by irradiation. However, our experiments proved that this was not the case. The epoxy radicals of epoxy compounds such as AGE, PGE, and Epicote 812 were found to be more or less radiation-resistant, and the majority of them remain unchanged by an irradiation dose of  $1 \times 10^7$ r.

So we believe that when an epoxy monomer such as MGE is radiation-grafted to another polymer, the greater part of its epoxy radicals remain

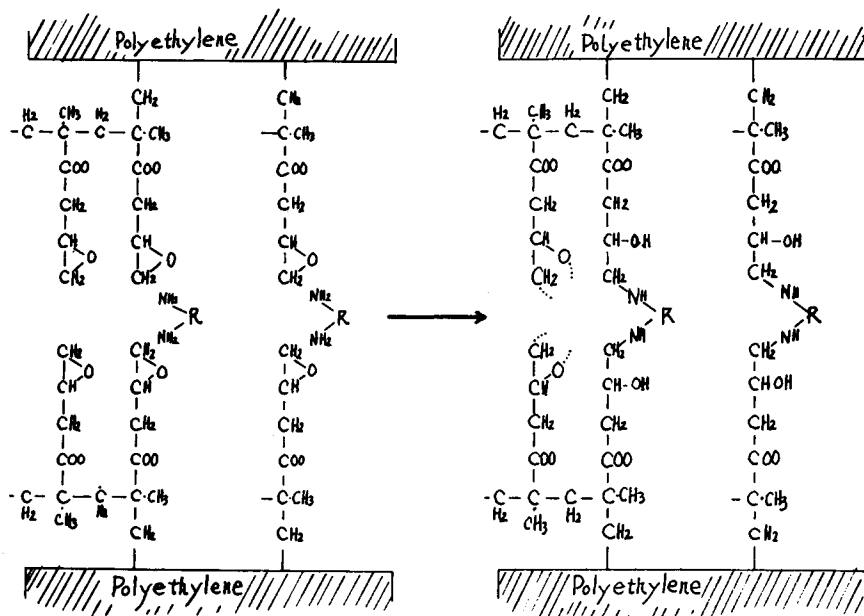


Fig. 6. Crosslinking in the grafted polyethylene.

unchanged. This is proved in Figures 4 and 5, by the presence of absorption of epoxy radicals in the region of  $800\text{--}950\text{ cm.}^{-1}$ .

The epoxy radicals grafted to the polymer are reactive, so that when epoxy resin adhesives containing amine hardener are coated to them, grafted epoxy radicals rings are opened and crosslinking takes place in the presence of amine hardener.

Figure 6 shows the state of crosslinking. According to the model, it is clear that two sheets of polyethylene are not only physically but also chemically bonded.

### References

1. Shrader, W. H., and M. J. Bodner, *Plastics Technol.*, **3**, 988 (1957).
2. Rossmann, K., *J. Polymer Sci.*, **19**, 141 (1956).
3. Kreidl, W. H., U.S. Pat. 2,632,921.
4. Chapman, R. N., and P. Colombo, *Nucleonics*, **13**, No. 10, 13 (1955).
5. Nelson, E. R., T. J. Kilduff, and A. A. Benderly, *Ind. Eng. Chem.*, **50**, 329 (1958).
6. Rieke, J. K., and M. Hart, *J. Polymer Sci.*, **C1**, 117 (1963).
7. Siggia, S., *Quantitative Organic Analysis via Functional Group*, Wiley, New York, 1963, p. 300.
8. Paquin, A. M., *Epoxyverbindungen und Epoxyharze*, Springer-Verlag, Berlin, 1958, p. 754.

### Résumé

On a irradié par rayons  $\gamma$  avec la dose totale de  $1 \times 10^{17}\text{--}2 \times 10^{18}$ , des composés époxy tel que l'allyl-glycidyl-éther, le phenyl-glycidyl-éther et l'Epicote 812, qui ne sont pas polymérisables par irradiation et on examine les décompositions des radicaux

époxy. En conséquence on trouve que les radicaux époxy sont plus ou moins résistants à la radiation et que leur plus grande partie demeure inchangée. On greffe par irradiation, les esters méthacryl-glycidyliques qui sont polymérisables par irradiation, au polyéthylène et au polytétrafluoroéthylène par irradiation simultanée des rayons  $\gamma$  et on controle le degré de greffage. Deux feuilles de polyéthylène ou de polytétrafluoroéthylène greffés par irradiation sont liées à des adhésifs à base de résine époxy contenant un polyamide comme durcissant et on examine la force de liaison. En conséquence, on prouve que la force de liaison du polymère greffé est plus grande que celle du non-greffé.

### Zusammenfassung

Epoxyverbindungen wie Allylcidyläther, Phenylglycidyläther und Epicote 812, welche durch Bestrahlung nicht polymerisierbar sind, wurden mit  $\gamma$ -Strahlen in einer Gesamtdosis von  $1 \times 10^7$  r- $2 \times 10^8$  r bestrahlt und die Zersetzung der Epoxyradikale untersucht. Es ergab sich, dass die Epoxyradikale mehr oder weniger strahlungsbeständig sind und ihr grösserer Teil unverändert bleibt. Methacryl-glycidylester, welche durch Bestrahlung polymerisierbar sind, wurden durch gleichzeitige Bestrahlung mit  $\gamma$ -Strahlen auf Polyäthylen und Polytetrafluoräthylen aufgepfropft und der Pflopfungsgrad bestimmt. Zwei Platten von strahlungsgepfropftem Polyäthylen oder Polytetrafluoräthylen wurden mit einem Epoxyharzkleber mit einem Polyamidhärter verklebt und die Klebefestigkeit untersucht. Es zeigte sich, dass die Klebefestigkeit des aufgepfropften Polymeren grösser als diejenige des nicht aufgepfropften ist.

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