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Radiation Effects
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MASTER

CURING PLASTICS WITH GAMMA RADIATION

W. L. Harper
B. Napier, Jr.

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UNION CARBIDE CORPORATION
Nuclear Division

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ABSTRACT

Several monomeric systems were polymerized with gamma radiation. Shear and compressive strengths were determined and correlated with the radiation dose.

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SUMMARY

Several monomeric systems were polymerized with gamma radiation and their strengths studied and correlated with the dose of radiation received. A number of these systems were found to undergo radiation polymerization readily, producing compacts with shear and compressive strengths comparable to those obtained by conventional curing methods. Compounds containing vinyl groups were found to be particularly radiation sensitive and certain epoxy systems cured readily. Diolifins appeared to be relatively insensitive to radiation.

INTRODUCTION

The polymerization of monomeric systems into hard, strong, and useful plastics with gamma radiation offers several potential advantages, namely: (1) the ability to incorporate plastics into heat-sensitive systems; (2) a means of manufacturing materials with improved physical and mechanical properties by virtue of a different polymerization mechanism induced by the radiation; (3) a method of producing more highly crosslinked polymers which would provide a higher coke yield on pyrolysis; and (4) a manufacturing method which perhaps, in some cases, could offer substantial economic advantages over the conventional methods.

These potential advantages have led to a study of the radiation polymerization of several monomeric systems with the emphasis being placed on a correlation of shear strengths of the irradiated samples with the radiation dose.

DISCUSSION OF THE STUDY

EXPERIMENTAL PROCEDURE

Practically all of the samples were irradiated at approximately 40° C in the Cobalt Storage Garden of the Oak Ridge National Laboratory, a storage facility having a cobalt-60 capacity of 300,000 curies. The dose rates for the samples irradiated in this facility ranged from 8.23×10^5 to 1.0×10^6 roentgens per hour. A cutaway drawing of this facility is presented in Figure 1.

A few samples were irradiated with a 300-curie cobalt-60 source at room temperature. These samples were irradiated at a dose rate of 4100 R/hr. Dose rate was not considered as a parameter in this study because of the comparatively few experiments run at the low rate.

The samples were prepared for admission to the irradiation facility by mixing the liquid monomers in the desired proportions and sending them in capped glass bottles. Those samples which were to be irradiated in the absence of air were sealed in glass containers in a vacuum at low temperatures. Polymerization inhibitors present in the monomers were not removed prior to irradiation because of the indeterminate waiting period before admission to the facility.

The irradiated samples were broken out of their glass containers and subsequently machined to size for ASTM shear⁽¹⁾ and compressive strength⁽²⁾ tests.

Additional correlation of the polymerization with radiation dose was provided in several cases, where the samples were still liquid after irradiation, by viscosity measurements and by determining the amount of the monomer consumed by gas-liquid chromatography.

Among the principal monomers considered were styrene, divinyl benzene, vinyl toluene, diallyl phthalate, maleic anhydride, 4-vinyl pyridine, epoxy ERLA-0510 [N,N-bis (2,3-epoxy propyl)-4-(2,3-epoxy propoxy) aniline], epoxy ERL-2258, and N-vinyl-2-pyrrolidone.

Shear strength was arbitrarily chosen as the parameter to serve as the basis for comparing the degree of polymerization obtained with gamma radiation on the various monomeric systems. It was found that the test specimens often broke at points on either side of the test point or sometimes even shattered under the test load. This breakage at different points on the test specimen is believed to be due to inconspicuous flaws in the samples and possibly accounts for some of the scatter in the data seen in the graphs. Despite the random breakage, the method appeared to provide a reasonable comparison of the strengths of the various systems.

Figure 1. COBALT STORAGE GARDEN AT THE OAK RIDGE NATIONAL LABORATORY.

While shear strengths provided the principal index of the degree of polymerization, some additional data were obtained. A series of compressive strength tests was also performed on several of the systems. In general, the available data suggest that compressive strengths might be less sensitive to radiation dose than shear strengths.

On several of the samples which had received relatively mild radiation doses, viscosities were determined as another means of indexing the degree of polymerization; and, on some of these samples, the percent of monomer consumed was determined by gas-liquid chromatography. These chromatographic analyses provided a means for estimating the number of monomer molecules polymerizing per 100 electron volts (ev) of radiation (termed the G value). The G value was estimated according to the equation of Gutzke and Yarko:⁽³⁾

$$G_{(\text{polymer})} = \frac{N \times \text{Moles of Monomer Going to the Polymer per Gram}}{I \times C},$$

where:

N is Avogadro's number, and

I represents the dose in roentgens equivalent physical (rep).

C is the factor that converts rep to 100 ev/g.

In this study the roentgen was considered equivalent to the rep.

CURING THE PLASTICS

Copolymers of Styrene

The radiation polymerization of the styrene monomer,

has been well documented,^(4, 5) and it was chosen as the major component in several copolymerization experiments. A mixture of styrene with seven parts per hundred parts resin (phr) of divinyl benzene (DVB) was found to polymerize readily with gamma radiation to produce a hard, translucent material. An example is shown in Figure 2. The divinyl benzene used,

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Figure 2. RADIATION-POLYMERIZED STYRENE + 7 PHR DIVINYL BENZENE.

was a 55 percent mixture of the three isomers (the meta isomer being the predominant one) with the three isomers of ethyl vinyl benzene.⁽⁶⁾

Correlation of the shear strengths with the radiation dose for this styrene copolymer is indicated in the graph of Figure 3. The data show a rather narrow range of shear strengths (6000 to 8000 psi) and suggest an optimum radiation dose of about 2×10^8 R. Doubling the amount of DVB or irradiating in a vacuum had no noticeable effect. Use of such free-radical catalysts as benzoyl peroxide or 2, 2'-azobis (2-methylpropionitrile) had no apparent effect.

Figure 3. CORRELATION OF SHEAR STRENGTHS WITH RADIATION DOSE FOR STYRENE + 7 PHR DIVINYLBENZENE.

Radiation dosages of less than 1×10^7 R produced incompletely cured specimens. Data on the samples receiving relatively small doses of radiation are included in Table 1. It can be seen that there was no change in the viscosity of the material at doses of 5×10^5 R and below, indicating a negligible amount of polymerization. Results of gas-chromatographic determinations of the amount of the styrene monomer consumed appear rather erratic at the lower doses; and, consequently, the resultant G values probably have no significance.

The G values determined at 3×10^6 and 5×10^6 R, radiation doses at which considerably more polymerization occurred, should provide a considerably better index of the sensitivity of the system to radiation and also provide a basis for comparison with other systems. Care must be exercised in using G values for comparison purposes since they depend on a number of physical factors, including dose rate, viscosity, and temperature.⁽⁷⁾

Available compressive-strength data for the styrene-DVB system is included in Table 2.

A few experiments were performed using materials other than the 55 percent DVB to copolymerize with styrene. Results of the shear tests on these irradiated specimens are summarized in Table 3. The data suggest that styrene-methyl methacrylate copolymers of moderate strengths can be prepared with relatively moderate radiation

Table 1
EXAMINATION OF PARTIALLY POLYMERIZED SYSTEMS

System	Radiation Dose (R)	Viscosity at 25° C (centistokes)	Monomer Consumed (mol %)	Estimated G Value
Styrene + 7 phr DVB	0	0.81	0	-
	1.6×10^4	0.83	2.1	1.5×10^4
	9.5×10^4	0.81	5.8	6.8×10^3
	2.0×10^5	0.80	3.7	2.1×10^3
	2.9×10^5	0.83	2.6	1.0×10^3
	5.0×10^5	0.83	4.8	1.1×10^3
	3.0×10^6	10.8	15.7	5.8×10^2
	3.0×10^6	-	13.1	4.9×10^2
	5.0×10^6	-	32.3	7.2×10^2
DAP + 10 phr Maleic Anhydride	0	8.2	0	-
	1.6×10^4	8.2	-	-
	9.5×10^4	7.9	-	-
	2.0×10^5	8.0	-	-
	2.9×10^5	1.57	-	-
4-Vinyl Pyridine	0	1.30	0	-
	1.6×10^4	1.30	-	-
	9.5×10^4	1.32	-	-
	2.0×10^5	1.33	-	-
	2.9×10^5	1.32	-	-
	5.0×10^5	2.15	5.1	1.1×10^3
	1.0×10^6	-	9.3	1.0×10^3
	3.0×10^6	39.0	23.3	0.9×10^3
2,4-Hexadiene	5.0×10^7	0.77	6.1	17
2,4-Hexadiene	2.5×10^8	-	44.1	25
1,5-Hexadiene	2.5×10^8	-	39.3	22
2,5-Dimethyl-2,4-Hexadiene	2.5×10^8	-	11.2	5
1,5-Pentadiene	5.0×10^7	0.69	19.3	66
3-Hexyne	2.5×10^8	-	27.8	16
Phenyl Acetylene	2.5×10^8	-	27.0	12
2-Allyl Phenol	2.5×10^8	-	61.4	21

doses and that vinyl toluene is inferior to DBV for copolymerization with styrene. The homopolymerization of styrene also produced inferior specimens.

Vinyl Toluene-Divinyl Benzene Copolymer

A monomer as similar to styrene as vinyl toluene, with the methyl group in the meta or para position:

Table 2
COMPRESSIVE STRENGTHS OF RADIATION-CURED PLASTIC SPECIMENS

Radiation Dose (R)	System						
	Styrene + 7 phr DVB	V-Pyrol(1)	ERLA-0510 + 137 MNA	Vinyl Toluene + 7 phr DVB	DAP(2)	4-Vinyl Pyridine	DAP + 10 phr Maleic Anhydride
5×10^5	-	18,191	-	-	-	-	-
1×10^6	-	21,894	-	12,576 ⁽¹⁾	-	-	-
	-	22,751	-	-	-	-	-
5×10^6	-	21,512	-	-	-	-	-
	-	21,309	-	-	-	-	-
5×10^7	-	20,852	-	14,340	-	18,746	-
	-	21,563	-	-	-	19,000	-
7.5×10^7	-	-	-	14,115	-	-	-
	-	-	-	14,305	-	-	-
1×10^8	14,170	22,400	20,800	14,655	23,163	17,829	26,800
	-	22,100	19,800	-	23,061	18,186	28,700
	14,397	21,867	-	14,345	-	-	-
	-	19,990	-	13,698	22,755	-	-
2.5×10^8	14,300	-	20,700	14,800	-	19,400	26,300
	14,100	-	18,600	14,800	16,000	19,200	27,300
	-	-	-	19,969	21,700	-	-
5×10^8	-	-	11,900	14,935	28,000	-	-
	13,130	-	18,300	14,910	25,900	-	-
	13,965	-	-	-	-	-	-
7.5×10^8	-	-	-	-	19,400	-	-

(1) 0.1% 2,2'-azobis [2-methyl propionitrile] used as a catalyst.

(2) 0.1% benzoyl peroxide used as a catalyst.

would be expected to exhibit similar radiation polymerization characteristics. This prediction was found to be true in the radiation copolymerization with DVB, as illustrated in Figure 4. However, additional data are needed to see if an optimum radiation dose exists, as is implied with the styrene-DVB system in Figure 3.

The compressive-strength data for this system are included in Table 2 and show that the copolymer exhibits comparatively moderate strengths and is seemingly insensitive to radiation doses over a wide range.

Table 3
SHEAR STRENGTHS OF OTHER RADIATION-POLYMERIZED COPOLYMERS OF STYRENE

Radiation Dose (R)	Shear Strength (psi)					
	Styrene (homopolymer)	Copolymer				
		Methyl Methacrylate (10 phr)	Vinyl Toluene ⁽¹⁾ (10 phr)	Divinyl Ether of 1,4-Butanediol (10 phr)	Isoprene ⁽²⁾ (10 phr)	1,5-Hexadiene (10 phr)
2.5×10^7	-	2710	-	-	-	-
5×10^7	1705	4370	-	-	-	-
	-	4400	-	-	-	-
1×10^8	1710	3020	2090	-	-	-
	-	2480	2690	-	-	-
2.5×10^8	-	-	-	-	1035	-
	-	-	2320	-	1760	-
3.0×10^8	-	1600	-	-	-	-
5×10^8	-	-	-	2430	1940	4440
7.5×10^8	1800	1580	4490	-	-	-
	-	-	2320	-	-	-
1×10^9	-	-	4300	-	-	-

(1) 0.1% benzoyl peroxide used as a catalyst.

(2) Irradiated in a vacuum.

Figure 4. CORRELATION OF SHEAR STRENGTHS WITH RADIATION DOSE FOR VINYL TOLUENE + 7 PHR DIVINYLBENZENE.

Homopolymerization of the Vinyl Pyridines

Two vinyl pyridines, 2-vinyl and 4-vinyl pyridine, are monomers and are similar in structure to styrene:

Shear strengths obtained on radiation-cured specimens of these two materials are given in Figure 5. It can be seen that compacts of relatively high shear strengths were produced at comparatively moderate radiation doses, particularly in the case of the 4-vinyl pyridine. The more favorable position of the vinyl group relative to the nitrogen in the 4-vinyl pyridine is undoubtedly responsible for its superior strength. Compressive strengths obtained on the 4-vinyl pyridine are included in Table 2; a few viscosities and G values for 4-vinyl pyridine are found in Table 1.

Figure 5. CORRELATION OF SHEAR STRENGTHS WITH RADIATION DOSE FOR 2-VINYL AND 4-VINYL PYRIDINE.

By comparing these values with those obtained for the styrene-DVB system, it can be seen from the viscosity data that significant polymerization occurred at considerably lower radiation doses than in the case of the styrene-DVB system. This fact is reflected in the higher G values obtained for the 4-vinyl pyridine as well as in the higher shear and compressive strengths obtained. Possibly the amine group functions as a catalyst in the vinyl pyridines.

N-Vinyl-2-Pyrrolidone

Another monomer containing a vinyl group which received attention was N-vinyl-2-pyrrolidone (V-Pyrol):

This monomer, catalyzed with 0.1 percent azobis (2-methylpropionitrile) was found to homopolymerize readily with rather low radiation doses to produce specimens with relatively high shear and compressive strengths. These data are presented in Figure 6 and Table 2. Some difficulty was encountered in producing V-Pyrol specimens free of gas bubbles; and, as pointed out earlier, inconspicuous flaws such as tiny bubbles may be responsible for some of the data scatter seen in Figure 6. The data in Figure 6 do suggest, however, that a rather low optimum radiation dose for the monomer does exist at approximately 5×10^6 R and that higher doses result in polymer deterioration.

Shear strengths were also determined on irradiated specimens of V-Pyrol containing 25 phr phenol. These data are included in Table 4 and are seen to be somewhat lower than that obtained for the pure monomer. Since the two components are known to react⁽⁸⁾ by the reaction,

Figure 6. CORRELATION OF SHEAR STRENGTHS WITH RADIATION DOSE FOR N-VINYL-2-PYRROLIDONE + 0.1 PERCENT AZOBIS (2-METHYLPROPIONITRILE).

the lower shear strengths would seem reasonable in light of the loss of vinyl groups.

Diallyl Phthalate-Maleic Anhydride Copolymer

Radiation polymerization of the system diallyl phthalate (DAP) + 10 phr maleic anhydride:

Diallyl Phthalate

Maleic Anhydride

resulted in translucent, hard specimens with comparatively high shear and compressive strengths. The shear strengths are shown in Figure 7; the compressive data are

Table 4
SHEAR STRENGTHS OF MISCELLANEOUS RADIATION-CURED
PLASTIC SYSTEMS

System	Radiation Dose (R)	Shear Strength (psi)
ERL-2258 + 20 phr	5×10^7	6285
m-Phenylenediamine	1×10^8	8700
	2×10^8	6480
	2×10^8	4680
	3×10^8	8510
	3×10^8	6680
DAP + 0.1% Benzoyl Peroxide	5×10^8	8470
	5×10^8	8140
	5×10^8	7215
	7.5×10^8	6620
	1×10^9	7615
	7.5×10^8	7200
DAP + 20 phr	7.5×10^8	7380
Allyl Glycidyl Ether	7.5×10^8	7200
	5×10^7	2530
55% Divinyl Benzene + 0.1% Benzoyl Peroxide	5×10^7	2980
	1×10^8	2400
	1×10^8	2500
Vinyl Toluene	1×10^9	3440
	1×10^8	3600
Divinyl Ether of 1,4-Butanediol	1×10^8	3400
	2.5×10^8	3700
	2.5×10^8	4000
	5×10^7	5255
	5×10^7	5350
	5×10^7	5410
V-Pyrol + 25 phr Phenol	1×10^8	4910
	2.5×10^8	6500
	2.5×10^8	5480
	2.5×10^8	5700
	5.0×10^8	7230

included in Table 2. The data in Figure 7 indicate that a relatively high radiation dose is necessary to insure high strengths, but no polymer deterioration is indicated at doses as high as 1×10^9 R. Irradiation in a vacuum did not appear to influence the results.

Both the compressive and shear strengths obtained on this copolymer were, in general, slightly higher than those obtained on the homopolymerization of DAP. The compressive strengths obtained on the DAP are tabulated in Table 2; the shear strengths are included in Table 4.

Epoxy ERL-2258

This difunctional epoxy of unknown structure was first irradiated with its vendor-recommended curing agent, m-phenylenediamine. Very brittle specimens resulted, exhibiting no strength. Some preliminary irradiation experiments have been performed using 4-vinyl pyridine as the curing agent. The results are quite encouraging, as indicated in Figure 8. Not only should the 4-vinyl pyridine induce an amine cure of the epoxy, but it should also undergo polymerization.

Epoxy ERLA-0510

The system ERLA-0510 + 137 phr methyl nadic anhydride (MNA):

ERLA-0510

[N, N bis(2, 3-epoxy propyl)-4-(2, 3-epoxy propoxy) aniline]

Methyl Nadic Anhydride
(MNA)

polymerized readily with moderately high radiation doses to produce specimens exhibiting good shear and compressive properties. The correlation of shear strengths with radiation dose is shown in Figure 9; the compressive data are included in Table 2. The data in Figure 9 again suggest polymer deterioration at the higher radiation doses. This suggestion is further exemplified visually in Figure 10 by comparing the appearance of the specimens. Considerable gas evolution appears to have occurred with the specimen HNP-119 receiving a dose of 1×10^9 R. Furthermore, it appears that radiation damage, or polymer deterioration, is inhibited by the use of allyl glycidyl ether (AGE) as a diluent.

Figure 7. CORRELATION OF SHEAR STRENGTHS WITH RADIATION DOSE FOR DIALLYL PHTHALATE + 10 PHR MALEIC ANHYDRIDE.

Figure 8. CORRELATION OF SHEAR STRENGTHS WITH RADIATION DOSE FOR ERL-2258 + 50 PHR 4-VINYL PYRIDINE.

Figure 9. CORRELATION OF SHEAR STRENGTHS WITH RADIATION DOSE FOR EPOXY ERLA-0510 + 137 PHR MNA.

As in the case of epoxy ERL-2258, some preliminary experiments have been made using 4-vinyl pyridine rather than MNA as the curing agent. The available results are promising and are presented in Figure 11.

Data obtained on other monomers and systems are included in Tables 1 and 4. G values (Table 1) obtained on various other hydrocarbons and related monomers suggest that these substances, diolifins in particular, are comparatively poor candidates for radiation polymerization.

COKE YIELDS ON PYROLYSIS

A number of irradiated samples were pyrolyzed very slowly in argon to 1100° C to determine their coking values. The results obtained are tabulated in Table 5. No striking increases in coke yields by virtue of the high-dose radiation polymerization were noted.

SUMMARY

In summary it can be stated that the experimental evidence obtained in the systems studied indicates that radiation polymerization yields products of good quality, but

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Figure 10. EFFECT OF ALLYL GLYCIDYL ETHER AS A DILUENT ON THE RADIATION-POLYMERIZED ERLA-0510-METHYL NADIC ANHYDRIDE SYSTEM.

the exhibited test properties were not found to be markedly superior to those obtained by the conventional polymerization means reported by the various vendors or obtained by laboratory experiment. However, the ease of polymerization by radiation was considerably greater than the conventional methods in many cases studied.

The comparable shear and compressive strengths and the relatively unimpressive coke yields obtained do not suggest that a different polymerization mechanism is occurring by virtue of the radiation.

While the systems studied did not appear to yield vastly superior materials on radiation polymerization, the possibilities are far from exhausted and further investigation is certainly warranted.

Figure 11. CORRELATION OF SHEAR STRENGTHS WITH RADIATION DOSE FOR EPOXY ERLA-0510 + 137 PHR 4-VINYL PYRIDINE.

Table 5
COKE YIELDS OBTAINED ON THE PYROLYSIS
OF CURED PLASTIC SYSTEMS

System	Radiation Dose (R)	Coke Yield (%)
DVB	0 (heat cure)	31.1
	1 x 10 ⁹	31.4
	1 x 10 ⁹	41.6
	1 x 10 ⁹	31.9
ERLA-0510 + 137 phr MNA	1.5 x 10 ⁹	36.2
	2 x 10 ⁹	36.8
V-Pyrol	1 x 10 ⁹	23.1
Vinyl Toluene	1 x 10 ⁹	11.8
	1 x 10 ⁹	13.4
Furfuryl Alcohol- 4% Maleic Anhydride	0 (heat cure)	43.9
	1 x 10 ⁹	51.6
Dicyclopentadiene	1 x 10 ⁹	25.7
Styrene + 10 phr Isoprene	5 x 10 ⁸	8.8
Styrene + 25 phr 1,5-Hexadiene	5 x 10 ⁸	9.6

CONCLUSIONS

A number of conclusions can be drawn from this study:

1. A number of monomeric systems have been found to undergo radiation polymerization readily to produce polymers with strength properties comparable to those obtained with conventional polymerization methods.
2. The vinyl pyridines and N-vinyl-2 pyrrolidone required the least amounts of radiation to produce polymers of relatively high strengths.
3. The diallyl phthallate + 10 phr maleic anhydride, styrene + 7 phr divinyl benzene, and epoxy ERLA-0510 + 137 phr methyl nadic anhydride systems also produced high-strength polymers at somewhat higher radiation levels.
4. The data indicate there is an optimum radiation dose for several systems. At higher doses, polymer deterioration appears to be initiated.
5. Generally, shear strengths appear to be slightly more radiation sensitive than compressive strengths.
6. Preliminary experiments on the radiation polymerization of several diolifins indicate that they are relatively insensitive to gamma radiation.

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