

Radiation Crosslinking of Vinyl Chloride-Vinyl Stearate Copolymer

A. A. MILLER

Research Laboratory, General Electric Company, Schenectady, New York

Earlier papers from this laboratory have described the radiation chemistry of polyvinyl chloride¹ and a process for crosslinking externally plasticized PVC by controlled electron-irradiation in the presence of small amounts of a tetrafunctional monomer, such as a dimethacrylate.² It was shown that in plasticized PVC, this radiation-crosslinking process produced increased strength, particularly at temperatures above 100°C., without noticeable impairment of the thermal and oxidative stability of the material. In the present paper this method is applied to an internally plasticized PVC, a copolymer of vinyl chloride and vinyl stearate.

EXPERIMENTAL

The original preparation, properties, and suggested uses of vinyl chloride-vinyl stearate copolymers have been described in publications from the Eastern Regional Research Laboratory, U.S. D. A.^{3,4} For this work, the flexible vinyl chloride-30% vinyl stearate copolymer, prepared by suspension polymerization, was obtained from the J. P. Frank Chemical Company. Combustion analysis of the material gave 50.8% C, 7.3% H, and 38.4% Cl, indicating that the vinyl stearate actually comprised about 32 wt.-% or 8.8 mole-% of the copolymer. Thus, the average composition was about 10 vinyl chloride units per vinyl stearate unit.

Attempts to measure the weight-average molecular weight, \bar{M}_w , by light scattering in benzene, toluene, or tetrahydrofuran solvents were unsuccessful because of complications due to association. Osmotic measurements in benzene at 25°C. as a function of concentration gave $\bar{M}_n = 49,800$ at 0.4% and 44,100 at 0.2%, which on extrapolation yielded a value of $\bar{M}_n = 39,400$ at zero concentration. Since the molecular weights of vinyl chloride and vinyl stearate are 62.5 and 310.5, respectively, we obtain $DP_n = 465$ for the number-average

degree of polymerization, which is similar to the value of 557 reported for a suspension copolymer of approximately the same composition in the original work.³

The ethylene diacrylate (EDA) and polyethylene glycol dimethacrylate (Monomer MG-1) were obtained from the Borden Chemical Company and Union Carbide Chemicals Company, respectively. For most of the work, ethylene dimethacrylate (EDMA), obtained from Sartomer Resins, Inc., was used. This monomer was a colorless fluid containing 0.006% hydroquinone inhibitor. The inhibitors were not removed from any of the monomers prior to use.

The stabilizer employed was Dythal, a dibasic lead phthalate (National Lead Company) and the fillers were Vulcan-9 carbon black and Cab-O-Sil compressed silica, both from Godfrey L. Cabot, Inc.

The vinyl chloride-30% vinyl stearate copolymer (henceforth designated as PVC-S) can be processed at 95-100°C. and gives a clear, flexible sheet resembling low-density polyethylene. The PVC-S was compounded with the additives by milling at 95-100°C. for about 5 min. The liquid monomers were added dropwise from a pipet during milling. Sheets were pressed at 120°C. for 30 sec. in a preheated press.

For gel and swelling measurements 10-mil thick samples (4 × 4 cm.) were irradiated with 800 kv. (peak) electrons from a G. E. resonant transformer unit at a normal dose rate of 14 Mr./min. (Mr = 10⁶ r) at room temperature and under a nitrogen atmosphere. One-half of each sample was retained for subsequent heat-aging tests. Weighed samples, usually about 0.2 g., were extracted twice in 25-ml. volumes of dimethylformamide (DMF) in test tubes in a 90-95°C. water bath, each extraction for a period of 2 hr. with occasional vigorous shaking. The extracted gel was then swollen in DMF at room temperature, surface-dried, and quickly enclosed in an aluminum-foil envelope to

measure the swollen weight. The gel was dried by vacuum-pumping in a desiccator at room temperature for at least 18 hr. The gel yield is given by the ratio of the weight of the extracted dry gel and the weight of the original sample. The weight swelling ratio, S_w , is reported as the ratio of the swollen weight to the weight of the extracted, dried gel.

For the tensile measurements, samples 20-mil thick (2×2 in.) were stamped into test dumbbells with a standard die, 2×0.5 in. overall and 0.125 in. wide at the neck. Measurements were made on a recording Instron unit at 25 and 150°C. with a drawing rate of 0.5 in./min.

RESULTS

Gel Yields and Swelling Ratios

The gel yields and swelling ratios as a function of irradiation dose are listed in Table I and the gel yields shown in Figure 1 for PVC-S itself and for PVC-S containing 5 wt.-% of the monomer additives.

With no additive the irradiation dose required for incipient gelation is 3 Mr. For the same weight concentration, the EDMA monomer is considerably more effective than either monomer MG-1 or EDA in increasing the degree of crosslinking. As was the case with externally plasticized PVC

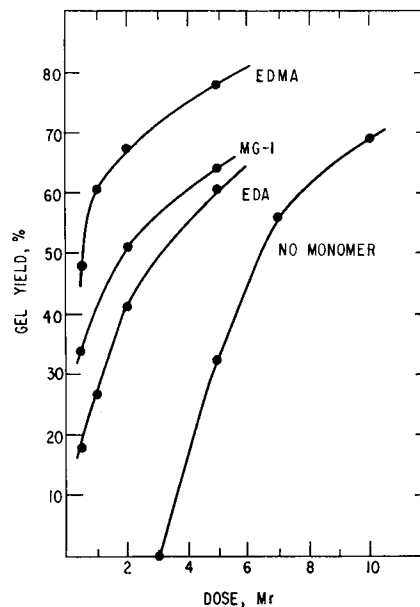


Fig. 1. Effect of monomers (5%) in radiation crosslinking of polyvinyl chloride-stearate.

reported previously,² the EDA monomer was apparently not completely compatible with the PVC-S as evidenced by crumbling of the polymer when the EDA was added during milling. Of the two dimethacrylates, the greater effect of the EDMA may be attributed, in part, to its lower molecular weight, giving a higher concentration of polymerizable double bonds for the same weight, and, in part, to the higher concentration of hydroquinone inhibitor (about 0.06%) contained in monomer MG-1. The addition of 5% EDMA to the PVC-S copolymer increases the radiation-crosslinking yield by almost 10-fold at the lower doses, as shown by a comparison of the relative doses required to produce equal gel yields (Fig. 1) and equal swelling (Table I). In the remainder of this work, only the EDMA monomer at a concentration of 5 wt.-% was used.

In Table I, it should be noted that for all cases the swelling ratios followed the normal pattern, i.e., decreasing as the irradiation dose and gel yield increased. This is in contrast with the abnormal, reverse behavior observed with a dimethacrylate additive in externally plasticized PVC.²

Table II shows further effects in the radiation crosslinking of PVC-S. The addition of the Dythyl stabilizer alone increases the crosslinking yield as indicated by higher gel yields and lower S_w at 5 and 10 Mr compared with the same doses in Table I. However, in the presence of EDMA monomer,

TABLE I
Gel Yields and Swelling for Polyvinyl Chloride-Stearate^a

| Additive | Dose, Mr | Gel yield, % | Swelling ratio S_w |
|-----------|----------|--------------|----------------------|
| None | 0 | 0 | — |
| | 2 | 0 | — |
| | 3 | Trace | — |
| | 5 | 32.4 | 13.9 |
| | 7 | 56.2 | 7.0 |
| | 10 | 69.0 | 5.0 |
| EDA (5%) | 0 | 0 | — |
| | 0.5 | 18.0 | — |
| | 1.0 | 27.1 | 13.9 |
| | 2 | 41.5 | 9.6 |
| | 5 | 60.5 | 5.9 |
| MG-1 (5%) | 0 | 0 | — |
| | 0.5 | 34 | 10.7 |
| | 2 | 51.0 | 7.0 |
| | 5 | 64.0 | 5.3 |
| EDMA (5%) | 0 | 0 | — |
| | 0.5 | 48.0 | 6.1 |
| | 1.0 | 60.5 | 5.2 |
| | 2 | 67.6 | 4.5 |
| | 5 | 77.8 | 3.4 |

^a All samples irradiated at room temperature at a dose rate of 14 Mr/min.

TABLE II
Effects of Dythral Stabilizer, Temperature, and Dose Rate on
Radiation Crosslinking of PVC-S

| Additives | Irradiation temp., °C. ^a | Dose rate, Mr/min. | Dose, Mr | Gel yield, % | Swelling ratio, S_w | |
|----------------------------|-------------------------------------|--------------------|----------|--------------|-----------------------|------|
| Dythral (3.5%) | R.T. ^a | 14 | 5 | 64.5 | 4.2 | |
| | | | 10 | 82.5 | 2.9 | |
| Dythral (3.5%) + EDMA (5%) | R.T. | 14 | 0.5 | 45.3 | 5.9 | |
| | | | 1 | 59.0 | 4.9 | |
| | | | 2 | 66.6 | 3.5 | |
| | | | 5 | 79.5 | 2.8 | |
| None | 100 | 14 | 2 | Trace | — | |
| | | | 5 | 64 | 7.4 | |
| Dythral (3.5%) | 100 | 14 | 2 | 27 | — | |
| | | | 5 | 78.5 | 3.9 | |
| EDMA (5%) | R.T. | 14 | 0.5 | 48.0 | 5.2 | |
| | 100 | 14 | 0.5 | 21.3 | >5.2 | |
| | R.T. | 0.14 | 0.5 | 46.5 | 4.0 | |
| EDMA (5%) + Dythral (3.5%) | R.T. | 14 | 0.5 | 44.7 | 6.1 | |
| | | | 100 | 0.5 | 38 | 12.0 |
| | | | 0.14 | 0.5 | 44.5 | 6.5 |

^a R.T. denotes room temperature (ca. °C.)

the Dythral has only a slight additional effect (lower S_w).

With no additives, irradiation of PVC-S at 100°C. produces more crosslinking than at room temperature, and with added Dythral stabilizer the crosslinking is increased even further. In fact, a 5-Mr dose under these conditions gives about the same gel yield and S_w as the same dose in a 5% EDMA sample at room temperature (Table I).

With 5% EDMA, with or without Dythral stabilizer, the data in Table II show that irradiation at 100°C. definitely decreases the amount of crosslinking compared to the same dose at room temperature (Table I). A 100-fold decrease in radiation intensity (dose rate), however, causes relatively little change in the crosslinking at room temperature.

The degree of radiation crosslinking of PVC-S with 5% EDMA and 3.5% Dythral is unaffected by added carbon black or silica fillers. The data for compositions containing 100 parts PVC-S and 25 parts filler (20 wt.-%) are listed in Table III. It was observed that, once gel was formed, all of the filler was retained in the gel structure during extraction with DMF. Therefore, the gel weights were corrected for the known weight of filler in the original sample and in the extracted gel, and the gel yields in Table III are based on the PVC-S polymer alone. With these corrections for filler content, the gel yields at equal doses are almost

TABLE III
Effect of Fillers on Radiation Crosslinking of PVC-S^a

| Filler | Dose, Mr | Gel yield, % | Swelling ratio S_w |
|--------------|----------|----------------|----------------------|
| None | 0 | 0 | — |
| | 0.5 | 49 | 4.6 |
| | 2.0 | 67.8 | 3.7 |
| | 5.0 | 81.0 | 2.6 |
| Carbon (20%) | 0 | 0 ^b | — ^b |
| | 0.5 | 40.3 | 5.7 |
| | 2.0 | 63.5 | 4.0 |
| | 5.0 | 78.5 | 3.0 |
| | 5 | 80.8 | 2.9 |
| Silica (20%) | 0 | 0 | — |
| | 0.5 | 50 | 6.1 |
| | 2 | 67 | 4.0 |
| | 5 | 80.8 | 2.9 |
| | 5 | 80.8 | 2.9 |

^a All samples contained 5% EDMA and 3.5% Dythral. Irradiations at room temperature and 14 Mr/min.

^b Gel yields and swelling ratios corrected for filler contents of initial samples and extracted gels.

identical for unfilled, carbon-filled, and silica-filled samples. Similarly, the weight swelling ratios, S_w , corrected for filler content, are only slightly different for the filled and unfilled samples at equal doses.

Estimate of Crosslinking Yield

For PVC-S itself with no additives the dose for incipient gelation is 3 Mr at 25°C. (Table I) and about 2 Mr at 100°C. (Table II). It had been shown in the original preparative work³ that for a suspension copolymer containing 8.5 mole-% vinyl stearate, $\bar{M}_w/\bar{M}_n \approx 4$. Assuming that the present material has about the same molecular weight distribution, from the measured value of \bar{M}_n we obtain $\bar{M}_w = 157,600$. Incipient gelation requires one crosslink for two initial "weight-average" molecules,⁵ and thus we estimate $G(x) \sim 2/100$ e.v. energy absorbed at 25°C. and $G(x) \sim 3$ at 100°C. These estimated radiation yields for crosslinking are appreciably higher than for rigid PVC homopolymer.¹ For the PVC-S copolymer containing 5% added EDMA monomer and irradiated at room temperature, incipient gelation occurs at less than 0.5 Mr (Table I), giving for these conditions an estimated crosslinking yield of $G(x) > 12$.

Post-Irradiation Effects

In the PVC-S copolymer, the presence of sequences of the $-\text{CH}_2\text{CH}(\text{Cl})-$ structure averaging 10 units in length, together with the possibility of entrapment of radicals in the polymer matrix,

suggested that under certain conditions post-irradiation reactions, notably dehydrochlorination, might occur. In PVC systems, post-irradiation dehydrochlorination is manifested by a change in visible color.¹ Such observations for the present PVC-S system will be described next.

Pressed films (25–30 mils thick) of PVC-S containing no additives were irradiated at several doses up to 20 Mr at room temperature and under a nitrogen atmosphere. Immediately after irradiation, only a slight discoloration (olive-green) was visible even at the highest dose. Upon storage in air at room temperature color developed slowly, and after a storage period of about one month the samples showed discoloration increasing with dose from lavender (3 Mr) through violet (5 to 7 Mr) to dark purple (20 Mr). Apparently, the thickness of these samples was sufficient to prevent the diffusion of oxygen at a rate rapid enough to inhibit the chain dehydrochlorination.

Post-irradiation color changes were examined in PVC-S films 20 mils thick containing 3.5% Dythal stabilizer and 5% EDMA monomer irradiated at 0.5, 1, 2, and 5 Mr at room temperature. There was little or no discoloration in any of the samples immediately after irradiation. Each sample was divided into three parts. One set was immediately annealed in test tubes in a 150°C. oil bath for 10 min. This annealing process produced only a faint discoloration in the 2 Mr sample and slightly more discoloration (light tan) in the 5 Mr sample, with no discoloration at all in the 0.5 and 1 Mr samples. After annealing, no further color changes occurred, even after prolonged storage at room temperature.

The second set of samples was outgassed in a vacuum system immediately after irradiation and stored in pure nitrogen at room temperature without annealing. The 0.5 and 1 Mr samples showed no change, while the 2 and 5 Mr samples gave discoloration increasing with dose and storage time. After five days, the 5 Mr sample (light purple) was further divided, and one portion was exposed to air. The color of this sample slowly faded to a pink tinge while the sample stored in nitrogen showed no further change.

The third set of samples, unannealed and stored in air at room temperature, developed a slight discoloration (faint pink) only for the 5 Mr dose. An explanation for these post-irradiation color changes in nitrogen and in air and the effects of added monomer at various doses has been presented in previous papers.^{1,2}

PVC-S samples without EDMA and with or without Dythal stabilizer, irradiated at 100°C. to a dose of 5 Mr, which produced considerable crosslinking (Table II), showed only a slight discoloration (light tan) with no further post-irradiation changes.

The effect of post-irradiation annealing on the degree of crosslinking was examined for the compositions shown in Table III irradiated at a dose of 0.5 Mr at room temperature. Following irradiation, each sample was divided into three parts. One set was annealed for 10 min. at 150°C. and a second set annealed for 30 min. The gel yields and swelling ratios for these samples (Table IV), when compared to those for unannealed controls, show that the amount of additional crosslinking induced by annealing at 150°C. was negligible, particularly for the shorter time. This conclusion is important in relation to a later discussion of tensile measurements at 150°C.

TABLE IV
Effect of Post-Irradiation Annealing on Crosslinking of PVC-S^a

| | Unfilled | | 20% Carbon | | 20% Silica | |
|----------------|-----------|-------|------------|-------|------------|-------|
| | Gel, % | S_w | Gel, % | S_w | Gel, % | S_w |
| No anneal | 50 | 5.4 | 40 | 6.7 | 42 | 5.3 |
| 150°C./10 min. | 52 | 5.2 | 42 | 5.8 | 51 | 4.9 |
| 150°C./30 min. | 61 | 4.8 | 48 | 5.0 | 56 | 4.8 |

^a All samples contained 5% EDMA and 3.5% Dythal; irradiated at room temperature to a total dose of 0.5 Mr.

Tensile Measurements

Tensile measurements were made on 20-mil samples of the compositions listed earlier in Table III, but irradiated only at 1 and 5 Mr. The results reported are the averages of measurements in quadruplicate, and agreement between the individual measurements was remarkably good. Figure 2 gives typical stress-strain curves at 25°C traced directly from the Instron chart and in proper scale. For the unirradiated PVC-S with no filler, the upper curve *A* refers to the original material and shows a high initial modulus. The addition of 5% EDMA monomer causes the tensile behavior shown by curve *B*, with a lower, more constant modulus. Radiation crosslinking at a dose of only 1 Mr produces a marked change in the stress-strain curves for filled and unfilled samples. The very high initial modulus up to a yield point suggests that the material has been converted to a

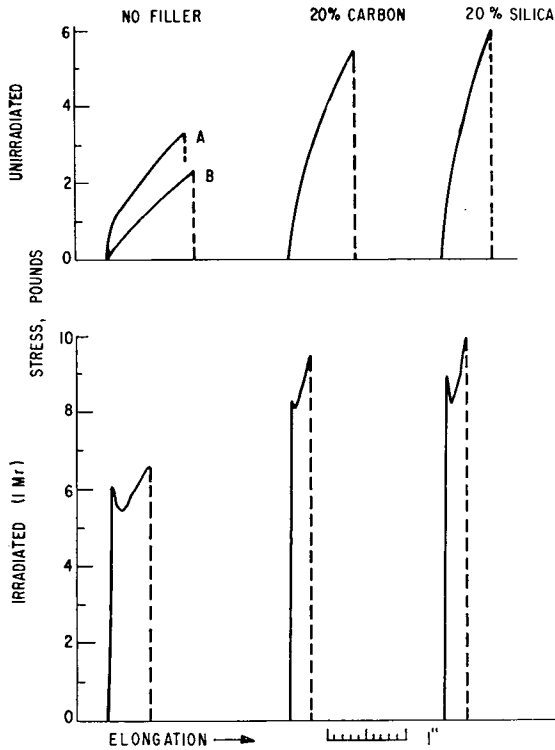


Fig. 2. Tensile curves for PVC-S at 25°C.

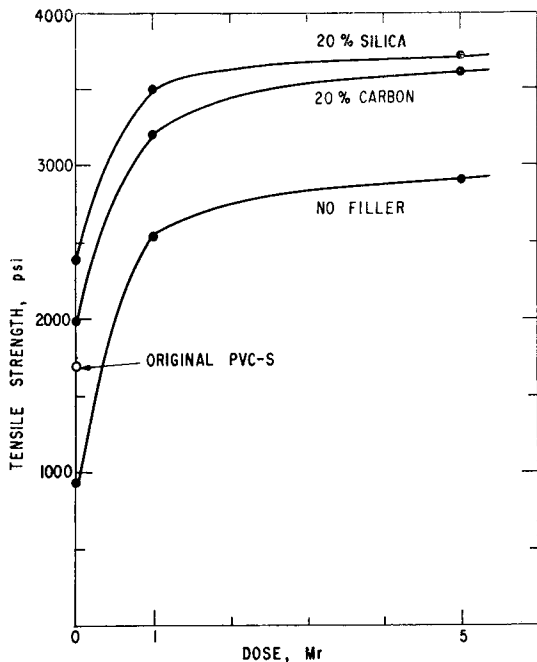


Fig. 3. Effects of filler and irradiation dose on tensile strength of PVC-S at 25°C.

more glasslike structure. For 5-Mr doses, the stress-strain curves had the same characteristics.

Figure 3 shows the ultimate tensile strength as a

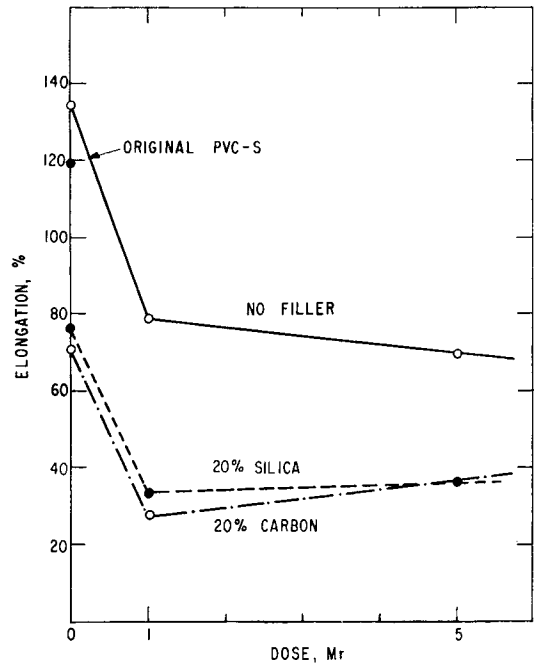


Fig. 4. Ultimate elongations for PVC-S at 25°C.

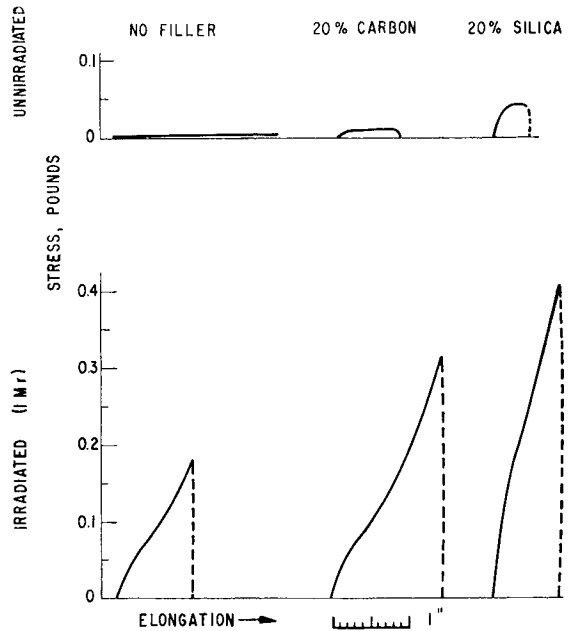


Fig. 5. Tensile curves for PVC-S at 150°C.

function of dose and filler. It should be noted that the original PVC-S, with or without Dythal stabilizer and without added EDMA, has a tensile strength of about 1700 psi; this is decreased to about 1000 psi when 5% EDMA is added, demonstrating the plasticizing effect of even a very low concentration of the monomer before crosslinking.

Radiation crosslinking causes parallel increases in strength for both the filled and unfilled material, the greatest change occurring up to 1 Mr. It is of interest, also, that both fillers have about the same effect on the tensile strength.

The elongations at break corresponding to the tensile strengths in Figure 3 are shown in Figure 4. Again, the greatest effect is at 1 Mr, and again the silica and carbon fillers show almost identical behavior. For the original PVC-S with no EDMA the elongation was about 120%.

For the tensile measurements at 150°C., typical stress-strain curves are shown in Figure 5, again drawn to the proper scale with regard to stress and elongation. The large increases in tensile strength produced by radiation crosslinking at 1 Mr are immediately apparent. Also, at this temperature, the crosslinked material no longer shows the glass-like characteristics which were observed at room temperature (Fig. 2). The tensile strengths at 150°C. as functions of irradiation dose and crosslinking are shown in Figure 6. (The values at 0 Mr were: no filler = 0.7 psi; 20% carbon = 3.8 psi; and 20% silica = 14.3 psi). With no filler, relatively little increase in tensile strength is achieved by irradiation beyond 1 Mr. However,

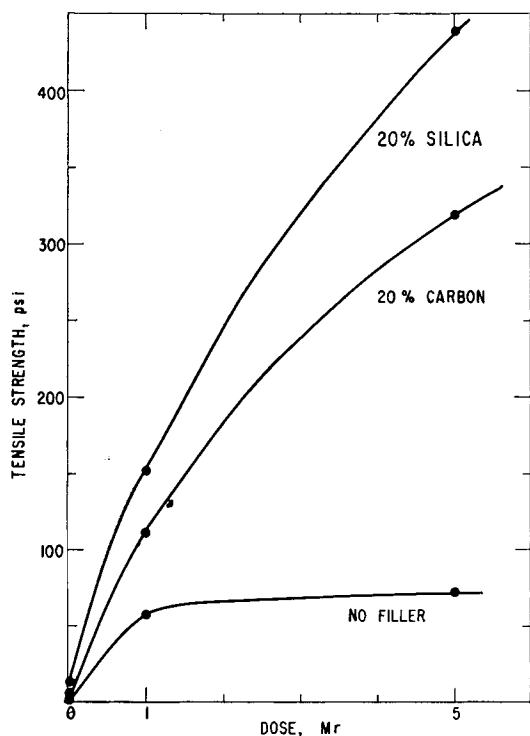


Fig. 6. Effects of filler and irradiation dose on tensile strength of PVC-S at 150°C.

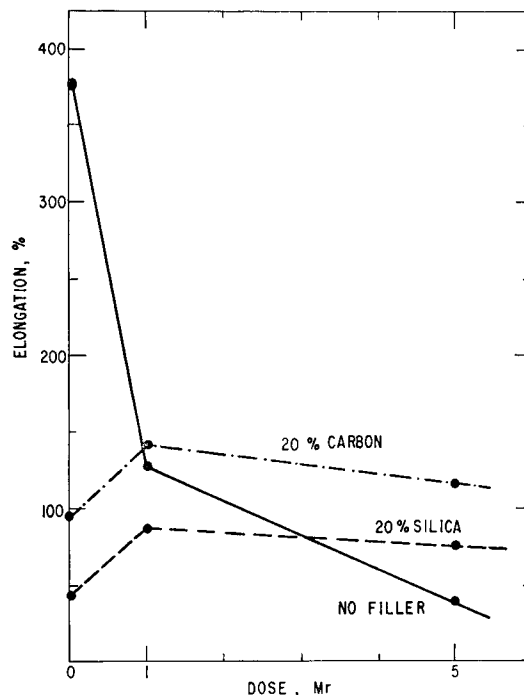


Fig. 7. Ultimate elongations for PVC-S at 150°C.

with the carbon and silica fillers the strengths continue to increase to remarkably high values at 5 Mr, and this is quite different from the behavior at room temperature (compare Fig. 3). For the ultimate elongations at 150°C. (Fig. 7), while the curve for the unfilled material behaves qualitatively the same as at room temperature (compare Fig. 4), the curves for the carbon- and silica-filled material show an increase rather than a decrease up to 1 Mr.

In the tensile measurements at 150°C. the possibility of additional post-irradiation crosslinking due to annealing at the 150°C. test temperature was considered, although gel measurements described earlier (Table IV) showed that for 10 min. at 150°C. in air (the approximate conditions for thermal equilibrium of the samples in the tensile tests) very little additional crosslinking occurred. This was verified by direct tensile measurements. Filled and unfilled samples (compositions in Table III) were irradiated at 5 Mr. One part of each sample was immediately annealed on a preheated glass plate in a 150°C. air-oven for 5 min. Averages of duplicate tensile measurements at room temperature for these annealed samples are compared to unannealed samples in Table V.

These tensile results, as well as the gel measurements in Table IV, show that annealing for short

TABLE V
Effect of Annealing at 150°C. for 5 Min. on Tensile Properties at 25°C.^a

| | Unfilled | | 20% Carbon | | 20% Silica | |
|-----------|----------------------------------|-----------------------|----------------------------------|-----------------------|----------------------------------|-----------------------|
| | Ten- sile strength, psi | Elonga- tion, % | Ten- sile strength, psi | Elonga- tion, % | Ten- sile strength, psi | Elonga- tion, % |
| No anneal | 2710 | 50 | 3950 | 30 | 3430 | 31 |
| Annealed | 2920 | 74 | 3425 | 35 | 3640 | 35 |

^a All samples irradiated to total dose of 5 Mr.

periods at 150°C. does not produce significant changes and certainly no great differences between the filled and unfilled samples.

It appears, therefore, that the difference in tensile behavior at 150°C. between the filled and unfilled materials (Figs. 6 and 7) is due to intrinsic properties and must be related to the relative contributions of crosslinking and filler reinforcement in the rubber state at this temperature. On the other hand, at 25°C. the physical state (i.e., glass or crystalline) is an additional factor which influences the tensile properties.

Peroxide Crosslinking

The complications inherent in conventional high-temperature, free-radical processes for crosslinking externally plasticized or unplasticized PVC have been mentioned previously.^{1,2} However, in the present internally plasticized PVC-S, which is undiluted by low molecular weight plasticizer and which contains long hydrocarbon (stearate) chains, crosslinking can be effected even with peroxide under the proper conditions.

In preliminary experiments, 1 and 3 wt.-% of dicumyl peroxide (Hercules) was milled into the PVC-S at 95–100°C. for about 5 min. There was no odor of acetophenone (one of the thermal decomposition products of the peroxide) and no discolora-

TABLE VI
Crosslinking of PVC-S with 3% Dicumyl Peroxide

| Additives | 170°C./5 min. | | 170°C./10 min. | |
|---------------------------------|---------------|-------|----------------|-------|
| | Gel, % | S_w | Gel, % | S_w |
| None | 30 | — | 35 | 19 |
| EDMA (5%) | 63 | 4.3 | 57 | 4.4 |
| Dythal (3.5%) | 94 | 2.5 | 94 | 2.3 |
| EDMA (5%) + Dythal (3.5%) | 92.5 | 2.1 | 93.3 | 1.7 |

tion of the polymer at this stage. Samples were press-cured in a preheated press at 170°C. for 15 min. Appreciable discoloration (tan to brown), increasing with the initial amount of peroxide, and severe blistering, presumably due to rapid gas evolution, resulted. Following this cure, the samples containing 1% peroxide were completely soluble in hot DMF, while those containing 3% peroxide gave only a trace of highly swollen, formless gel, showing that little or no crosslinking occurred under these curing conditions. Further experiments with added EDMA and Dythal stabilizer at cure times of 5 and 10 min. are listed in Table VI.

With 3% peroxide alone, only low yields of highly swollen gels resulted. The addition of EDMA increased the crosslinking. The Dythal stabilizer with or without EDMA, produced a very high degree of crosslinking, as shown by the high gel yields (>90%) and very low swelling ratios. Apparently, the Dythal stabilizer is an essential additive for the crosslinking of PVC-S with dicumyl peroxide. A reasonable explanation is that in this PVC-S system an acid-induced (HCl) ionic decomposition of the dicumyl peroxide competes with the thermal decomposition into free radicals, and only the latter are effective in the crosslinking.⁶ Presumably, the HCl formed by the dehydrochlorination during the high-temperature cure was scavenged by the Dythal stabilizer to sufficiently reduce the acid-catalyzed decomposition of the peroxide. Despite the high degree of crosslinking which can be achieved in PVC-S by the peroxide-Dythal system, it should be emphasized that in all cases significant decomposition also occurred, as evidenced by the discoloration (tan or brown) in the cured samples.

Finally, the effect of 5% EDMA monomer alone (without peroxide or stabilizer) in PVC-S was examined briefly. Samples pressed at 170°C. for 5 and 10 min. showed only a slight discoloration (light green) and were completely soluble in hot DMF. This not only shows that EDMA alone does not thermally cure the polymer but suggests also, that long shelf-lives at ordinary storage temperatures prior to irradiation may be expected for PVC-S compositions containing EDMA.

Aging Tests at 150°C

Four series of PVC samples were compared for discoloration and loss of flexibility in aging tests at 150°C. in an air-oven: (A) PVC-S containing 5% EDMA monomer and 3.5% Dythal stabilizer,

irradiated at 1 and 5 Mr; (B) PVC-S containing 3.5% Dythal and crosslinked with 3% dicumyl peroxide at 170°C. for 5 and 10 min.; (C) filled PVC-S samples with compositions and doses listed in Table III; (D) controls of PVC-S containing only 3.5% Dythal with no irradiation or crosslinking.

Initially, the unfilled samples which were radiation-crosslinked were white or slightly off-white, while the peroxide-crosslinked samples were tan or brown in color. When the samples were aged at 150°C. the rate of discoloration was lowest for the A series, and, of these, the 1 Mr sample showed a lower rate of discoloration than the 5 Mr sample. The silica-filled samples (C) discolored even more slowly than the unfilled (A) samples for the same irradiation doses. In the peroxide-cured materials (B), samples cured for 5 min. discolored more rapidly than those cured for 10 min. This could be attributed to a higher residual peroxide concentration following the 5 min. cure which, in the 150°C. aging test, would initiate a free-radical dehydrochlorination and consequent discoloration.

After 8 hr. at 150°C., all of the samples were uniformly discolored (brown) and underwent no further change. Further aging produced embrittlement uniformly at about 24 hr., in all of the unfilled and carbon-filled samples and somewhat sooner (20 hr.) in the silica-filled material.

It was concluded on the basis of these aging tests that the thermal and oxidative stability of PVC-S which was radiation-crosslinked at 1 Mr in the presence of 5% EDMA monomer was at least as good as that of unirradiated uncrosslinked controls of the same composition. The same conclusion had been made previously for radiation-crosslinked, externally plasticized PVC.²

CONCLUSIONS

The internally plasticized polyvinyl chloride-stearate copolymer has been shown to have properties which are superior to the conventional, externally plasticized PVC.^{3,4} However, for possible continuous or intermittent use at elevated temperatures, i.e., above 100°C., a serious limitation for both internally and externally plasticized PVC is loss of strength and thermoplastic flow. This limitation can be reduced or eliminated by proper crosslinking of the plasticized PVC.

Polyvinyl chloride-stearate can be crosslinked by chemical agents, such as polyfunctional amines with or without sulfur,⁴ and, as shown here, by

dicumyl peroxide. However, the high-temperature peroxide method, and presumably also the amine method, causes concurrent decomposition (dehydrochlorination). Crosslinking without decomposition can be achieved by irradiation under the proper conditions. Although the presence of a tetrafunctional monomer is not as essential for this polymer as for externally plasticized PVC,² it is still beneficial in lowering the dose required for crosslinking and minimizing post-irradiation changes. Without this additive, either post-irradiation annealing or irradiation at elevated temperature (100°C.) apparently is required to eliminate undesirable post-irradiation effects.

The crosslinking of polyvinyl chloride-stearate produces significant changes in physical properties both at room temperature and at 150°C. At the latter test temperature, crosslinking with filler reinforcement increases the tensile strength at least tenfold.

The aging tests at 150°C. suggest that the thermal and oxidative stability of PVC-S which has been radiation-crosslinked under the proper conditions compares favorably with that of unirradiated, uncrosslinked controls of similar compositions. It is not unlikely that improved chemical stabilizers for ordinary PVC, as they are developed, will be effective also in the radiation-crosslinked material.

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Synopsis

The crosslinking of internally plasticized polyvinyl chloride-stearate copolymer by irradiation with high-energy elec-

trons was studied. Based on gel yields and swelling as a measure of relative crosslinking, the effect of added tetrafunctional monomers, and of carbon black and silica fillers are discussed. Crosslinking by dicumyl peroxide at 170°C. even in the presence of a stabilizer, causes concurrent decomposition (dehydrochlorination) which is avoided in the radiation-crosslinking process. The heat stability of the copolymer is not impaired by radiation crosslinking under the proper conditions. Results of tensile measurements at 25 and 150°C. are given for the radiation-crosslinked copolymer with and without filler reinforcement.

Résumé

On a étudié le pontage d'un copolymère de chlorure et stéarate de polyvinyle plastifié sous l'effet d'une irradiation par des électrons de haute énergie. Sur la base du rendement en gel et du gonflement comme mesure du taux relatif de pontage on discute l'addition de monomères tétrafonctionnels, de noir de carbone et de charge à base de silice. Le pontage à l'aide de peroxyde de dicumyle à la température de 170°C cause, même en présence d'un stabilisateur, une décomposition concurrente (une déhydrochloration). On peut éviter cet inconvénient en utilisant les radiations comme agent de pontage. On n'altère pas la résistance à la chaleur

du copolymère par le pontage initié par les radiations ionisantes si l'on travaille dans des conditions appropriées. On donne des mesures de tension à 25°C et à 150°C pour un copolymère ponté par irradiation avec ou sans renforcement par une charge.

Zusammenfassung

Die Vernetzung eines Polyvinylchlorid-Stearat-Copolymeren mit innerer Weichmachung durch Bestrahlung mit hochenergetischen Elektronen wurde untersucht. Auf Grund der Gelausbeuten und der Quellung als Mass für die relative Vernetzung wird der Einfluss des Zusatzes von tetrafunktionellen Monomeren, von Russ und Kieselsäurefüllstoffen diskutiert. Vernetzung mit Dicumylperoxyd bei 170°C verursacht sogar in Gegenwart eines Stabilisators eine gleichzeitige Zersetzung (Dehydrochlorierung), die bei der Vernetzung durch Bestrahlung vermieden wird. Die Hitzebeständigkeit der Copolymeren wird durch die Bestrahlungsvernetzung unter geeigneten Bedingungen nicht beeinträchtigt. Dehnungsmessungen bei 25 und 150°C an strahlungsvernetzten Copolymeren mit und ohne Verstärkung durch Füllstoffe werden beschrieben.

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