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GEL PERMEATION CHROMATOGRAPHIC INVESTIGATION OF IRRADIATED COPOLYMERS

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SUMMARY

Hot melt samples of irradiated and non-irradiated ethylene–isobutyl acrylate copolymers and ethylene–vinyl acetate copolymers were examined with gel permeation chromatography and the gel content determined to investigate changes in polymer growth upon increasing radiation dosage. Variations in the molecular size and gel content of both copolymer systems studied suggested that the degree of cross-linking is inversely dependent upon the molecular size of the starting material and the rate of degradation is directly related to molecular size. It has been demonstrated that these techniques can be employed to determine the optimum initial molecular size and polymer composition for selection of a copolymer system for irradiation.

INTRODUCTION

Radiation studies have been reported most extensively for polyethylene and other polyolefins. Some general observations have been made with these systems which may act as a guide in the investigation of the effects of radiation for copolymers.

Radiation of polymeric materials can cause cross-linking (polymerization) and/or chain scission (degradation). KANG *et al.*[1] concluded that the cross-linking probability in polyethylene increases faster than the radiation dose while the chain scission probability remains directly proportional to dose. Based upon FLORY's equations for random cross-linking of a polymer[2], LYONS AND FOX[3] concluded that, at a specific molecular weight, the loss in material due to chain scission and to cross-linking will be exactly balanced by the gain due to scission of larger molecules provided the chain scission probability is relatively small compared with the cross-linking probability.

Cross-linking in polyethylenes is believed to involve carbon–hydrogen bond scission and subsequent coupling of resultant alkyl radical intermediates according to CHARLESBY[4,5]. He concluded that the radiolytic behavior of polyethylene and other polymers could be explained by assuming that both main-chain scission and cross-linking occur randomly along the polymer chain. More recently GEYMER[6] concluded, on the basis of kinetic considerations, that radiation-induced cross-linking of polypropylene involves free radicals.

The copolymer systems reported here, ethylene–isobutyl acrylate and ethylene–vinyl acetate, were investigated to aid in the application of radiation curing to commercial resins acceptable for coatings. Several interesting observations were made that define parameters to be considered in the selection of copolymer materials and radiation conditions to obtain optimum physical properties of the cross-linked copolymer. A study of relative molecular size distributions with gel permeation chromatography (GPC) and gel content of the irradiated copolymer is demonstrated to be of value in determining the conditions necessary for achieving optimum physical properties of the radiation products.

EXPERIMENTAL

Pressed films of copolymers consisting of ethylene–isobutyl acrylate and ethylene–vinyl acetate were cross-linked by irradiation with a cobalt-60 γ-radiation source and limited access to air. Composition effects were studied with films of similar molecular weight but varying monomer content. Effects due to differences in molecular weight were determined with films from resins of the same composition but of varying melt index.

Radiation dosages of 2.6, 10.6, and 22.3 Mrad were employed to cross-link the two different types of copolymers investigated, ethylene–isobutyl acrylate (Zetafax resins supplied by E. I. duPont Co.) and ethylene–vinyl acetate (Elvax resins supplied by Dow Chemical Co.). The copolymers were characterized as to composition, melt index, weight average ($\bar{A}_w$) and number average ($\bar{A}_n$) molecular size, percent crystallinity, and melting point. GPC was employed to determine $\bar{A}_w$ and $\bar{A}_n$ of the copolymers before irradiation and after each radiation dose. In addition, the gel content was determined and the observation of changes in the molecular size distribution parameters, $\bar{A}_w$ and $\bar{A}_n$, were compared with changes in gel content. These measurements were correlated with changes in physical properties investigated with an Instron Tester and included measurement of breaking stress (tensile strength), elongation at break, tensile modulus, and non-elastic deformation.

EQUIPMENT

Waters Associates Model 100 gel permeation chromatograph

GPC analyses were conducted with the copolymers dissolved in *o*-dichlorobenzene at 130°, with four columns in series packed with Styragel having exclusion limits of 10^6, 10^5, 10^4, 10^3 Å, respectively. The columns were calibrated with polystyrene standards having narrow molecular weight distributions.

Cobalt–60 source

Ten pencils of cobalt-60.

Ceric sulfate dosimeter

Film sections were extended between two points where equivalent dosage rates were observed and the total dosage was governed by exposure time.

Pasadena hydraulic press

Films of the polymers were made by pressing at a temperature of 300° F and

a pressure of 1880 lb./sq. in. They were cooled rapidly by running water through the platens of the press while the pressure was maintained. The films were placed between sheets of plate glass (3/64 in. thick) and sealed with pressure sensitive tape.

Instron tester Model TM

TEST METHODS

Gel content determination

A sample of polymer (1.25 g) was refluxed for 3 h with 150 ml of *o*-dichlorobenzene, cooled, and filtered through No. 41 Whatman paper with a Buchner funnel, washed with fresh solvent, and brought to the mark in a 250 ml volumetric flask. An aliquot was evaporated to dryness, placed in a vacuum oven at 60°C for 1 h, cooled and weighed. The gel content was calculated by difference based on the weight of polymer contained in the 25 ml aliquot of the filtered solution, and the weight of polymer contained in a 25 ml aliquot without filtering.

Tensile modulus

Determined with the Instron tester according to ASTM Method D-882.

Breaking stress and break elongation

Determined with the Instron tester in which samples of 2 in. gauge length were stretched 150 % of original elongation at a rate of 1 in. per min, retracted, and repeated for three full cycles.

Computer calculations were employed to tabulate and establish the statistical significance of the data on mechanical properties.

RESULTS

The unique finding with the ethylene–isobutyl acrylate series of copolymers is that molecular size begins to increase rapidly at 2.6 Mrad, forms gel at 10.6 Mrad, but on continued radiation exposure the gel disappears. This could be explained if the main chain scission referred to by CHARLESBY[4,5] occurred to the point where sufficient main chain fragmentation took place to break up the network structure of the gel. The observation of events which were followed with GPC curves are shown for sample Z-1278 (20 % IBA, 250 melt index (M.I.)) in Fig. 1 in which the curves are arranged so that their axes coincide. A fairly small fraction of high molecular size material can be seen before irradiation and an increase can be seen in the high molecular size end after irradiation at the 2.6 Mrad level. At 10.6 Mrad dosage, at which point gel formed, the high molecular size shoulder has disappeared. At 22.3 Mrad the gel fraction has disappeared and a distribution curve similar to the original material is observed including restoration of high and medium molecular size fractions. GPC indicates that cross-linking begins at low levels of irradiation. A gel is formed with continued radiation which is then degraded to almost restore the original system. The requirements for optimum radiation cross-linking was found to be a low molecular weight starting material (M.I. about 250) and an isobutyl acrylate content of 30 % or higher.

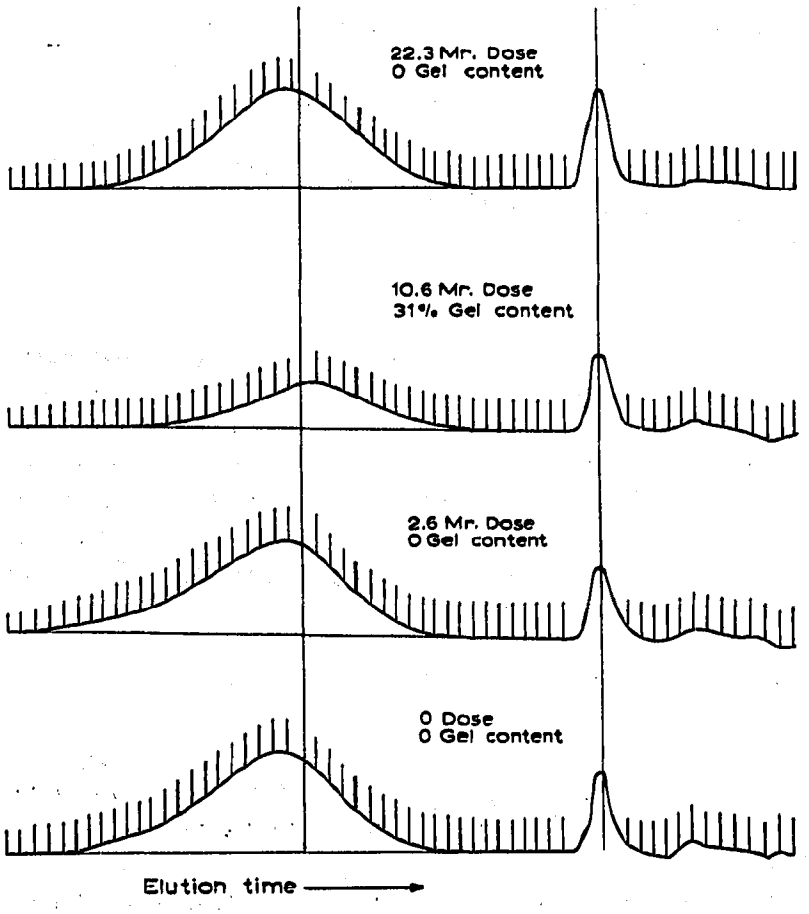

Fig. 1. GPC Molecular size distribution, ethylene–isobutyl acrylate copolymer γ-irradiated Dow Z-1278, 20% IBA, M.I. = 250.

GPC and gel content studies indicate a much lower degree of cross-linking at the extremes of molecular weight for the ethylene–vinyl acetate copolymers. The lowest molecular weight copolymer tested is probably too low in average molecular size to attain the proper size for gelation. The highest molecular weight copolymers tested are probably of too low mobility (similar to macro-Brownian movement) to allow access of active centers of adjacent molecules for cross-linking.

Ethylene–vinyl acetate copolymers having a vinyl acetate content of greater than 30 % but probably less than 42 % and in the molecular weight range 22–175 M.I. would be optimum for sensitivity to radiation.

Ethylene–isobutyl acrylate copolymers

The GPC data presented in Table I show that for the ethylene–isobutyl acrylate copolymers the highest weight average molecular size, $\bar{A}_w$, observed in *o*-dichlorobenzene solvent for each series of copolymers exists at a radiation dosage of 2.6 Mrad. A dramatic decrease in the weight average molecular size of the copolymer in solution is observed at the 10.6 Mrad level for the entire series of copolymers and is accompanied by the appearance of an insoluble portion (gel) as shown in Table II.

The next level of radiation dosage, 22.3 Mrad yielded a decrease in gel content for the three samples which contained gel at 10.6 Mrad. The gel content was observed

TABLE I

ETHYLENE–ISOBUTYL ACRYLATE COPOLYMERS: VARIATION OF WEIGHT AVERAGE MOLECULAR SIZE WITH RADIATION DOSAGE

Sample	*% IBA*	*M.I. (g/10 min)*	*Weight average molecular size ($\bar{A}_w$)*			
			Radiation dosage (Mrad)			
			None	*2.6*	*10.6*	*22.3*
Z-1278	20	250	3510	7 010	1510	2070
Z-1275	20	20	5540	16 700	2210	2770
Z-1270	20	2–3	7860	17 600	3490	3160
Z-1375	30	20	6880	21 500	2440	3870
Z-1370	30	2–3	8140	24 600	1330	2070

TABLE II

ETHYLENE–ISOBUTYL ACRYLATE COPOLYMERS: VARIATION OF GEL CONTENT WITH RADIATION DOSAGE

Sample	*% IBA*	*M.I. (g/10 min)*	*Gel content (%)*			
			Radiation dosage (Mrad)			
			None	*2.6*	*10.6*	*22.3*
Z-1278	20	250	0	0	30.9	0
Z-1275	20	20	0	0	12.8	0
Z-1270	20	2–3	0	0	0	0
Z-1375	30	20	0	0	2.2	16.0
Z-1370	30	2–3	0	0	3.5	0

to increase for sample Z-1375 (30 % isobutyl acrylate (IBA), 20 M.I.), which contains a higher isobutyl acrylate content (30 %), in the range from 10.6 to 22.3 Mrad. The weight average molecular size, $\bar{A}_w$, of this sample was also observed to increase significantly at the 22.3 Mrad radiation dosage compared with the 10.6 Mrad irradiated sample as shown in Table I. Sample Z-1370 (30 % IBA, 2–3 M.I.), which also has a higher isobutyl acrylate content, also exhibits a larger molecular size than the 20 % isobutyl acrylate samples in *o*-dichlorobenzene. The data indicate that molecular size increases with the isobutyl acrylate content upon irradiation.

Samples of series Z-1275 and Z-1375, each initially having a melt index of 20 (20 % and 30 % IBA respectively) exhibit a similar maximum gel content (13 % and 16 %) as shown in Table III. Sample Z-1278 which had a lower molecular size (M.I. 250

TABLE III

ETHYLENE-ISOBUTYL ACRYLATE COPOLYMERS: MAXIMUM GEL CONTENT OF IRRADIATED SAMPLES

Sample	*% IBA*	*M.I. (g/10 min)*	*Maximum gel content (%)*
Z-1278	20	250	30.9
Z-1375	30	20	16.0
Z-1275	20	20	12.8
Z-1370	30	2–3	3.5
Z-1270	20	2–3	0.0

and 20 % IBA) shows the highest gel content, 31 %, of the five samples investigated. This observation probably reflects greater tendency for the lower molecular weight starting material to increase in size.

Mechanical properties in general followed the cross-linking reaction. The variation of break stress (tensile strength) and gel content for sample Z-1278 with increased radiation dosage are seen in Fig. 2 to show correlation. It can be seen in Table IV that in general, the lower molecular weight polymers were observed to increase in strength with radiation. When the gel content of the lower molecular weight starting

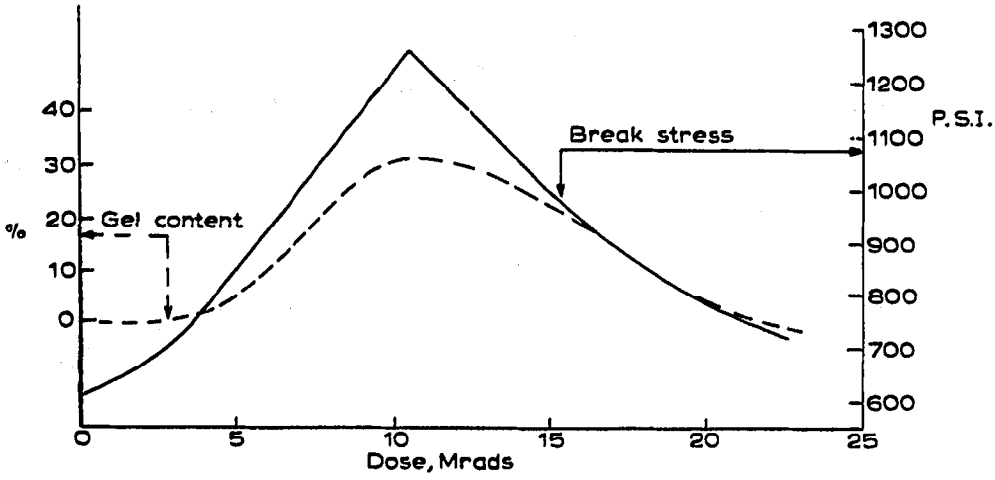

Fig. 2. γ-Radiation effect on breaking stress and gel content of ethylene–isobutyl acrylate copolymer. Dow Zetafax 1278, 20% IBA, M.I. = 250.

TABLE IV

ETHYLENE-ISOBUTYL ACRYLATE COPOLYMERS: EFFECT OF γ-IRRADIATION ON MECHANICAL PROPERTIES

Sample No.	*% IBA*	*Mole ratio E/IBA*	*M.I. (g/10 min)*	*Radiation dosage (Mrads)*	*Break stress (p.s.i.)*
Z-1270	20	18/1	2–3	0	2367
				2.6	2329
				10.6	2448
				22.3	2269
Z-1275	20	18/1	20	0	1571
				2.6	1691
				10.6	1683
				22.3	1751
Z-1278	20	18/1	250	0	635
				2.6	704
				10.6	1263
				22.3	735
Z-1370	30	11/1	2–3	0	2338
				2.6	2340
				10.6	2169
				22.3	2425
Z-1375	30	11/1	20	0	1284
				2.6	1406
				10.6	1409
				22.3	1387

material decreased or disappeared, a drop was observed in break stress but not back to the original level. It can be seen in Table IV that in general, the lower molecular weight polymers (Z-1278, Z-1275, and Z-1375) were observed to increase in strength with radiation up to the 10.6 Mrad dose level. The initially higher molecular weight samples, Z-1270 and Z-1370, showed slight but statistically significant losses in break stress at the 2.6 or 10.6 Mrad level.

The investigation of physical properties indicate that the higher initial molecular weight polymers are slightly adversely affected by irradiation while the lower initial molecular weight polymers show improvement in physical properties. In addition the copolymers which have a higher isobutyl acrylate content appear to be more susceptible to irradiation than those with lower isobutyl acrylate content. These findings corroborate the observations made with GPC and gel content studies.

Ethylene–vinyl acetate copolymers

The ethylene–vinyl acetate (VA) copolymers of varying initial molecular weight and varying composition generally showed an increase in molecular size with initial

TABLE V

ETHYLENE-VINYL ACETATE COPOLYMERS: MOLECULAR SIZE AND PERCENT GEL DATA

Sample No.	*VA (%)*	*M.I. (g/10 min)*	*Radiation dosage (Mrads)*	$\bar{A}_w \times 10^{-3}$	$\bar{A}_n \times 10^{-2}$	*Gel (%)*
E-40	39–42	45–65	0	3.83	9.92	0.0
			2.6	11.3	6.72	8.2
E-150	32–34	22–28	0	3.26	8.26	0.0
			2.6	4.63	7.38	23
E-210	27–29	340–370	0	1.69	5.47	0.0
			2.6	1.94	4.27	0.0
			10.6	1.74	6.83	1.2
			22.3	1.65	4.95	0.8
E-220	27–29	125–175	0	3.16	7.59	0.0
			2.6	4.51	7.05	3.5
			10.6	4.11	8.82	4.5
			22.3	2.49	5.16	33
E-240	27–29	22–28	0	3.79	8.16	0.0
			2.6	4.99	6.46	2.4
			10.6	3.44	5.72	6.3
			22.3	1.38	2.24	65
E-250	27–29	12–18	0	4.19	8.36	0.0
			2.6	5.01	6.99	0.0
			10.6	4.66	6.27	8.2
			22.3	6.44	6.48	5.6
E-260	27–29	5–7	0	5.14	1.21	0.0
			2.6	3.63	11.9	0.0
			10.6	5.61	6.93	2.2
			22.3	3.81	4.81	4.8
E-350	24–26	16–22	0	3.84	10.3	0.0
			2.6	3.53	9.89	0.0
E-460	17–19	2–2	0	5.78	11.8	0.0
			2.6	7.85	6.48	3.3

radiation at the 2.6 Mrad dosage level as shown in Table V. The next higher level of radiation dosage, 10.6 Mrad, generally showed a decrease in the molecular size of the copolymer in solution but was accompanied by an increase in the gel content. Sample E-250 (27-29 % VA, 12–18 M.I.) showed a drop in gel content between irradiation dosages of 10.6 and 22.3 Mrad. In the series of copolymers having the same composition (27–29 % VA), maximum sensitivity to irradiation was experienced in the medium to low molecular weight range. This can be seen for samples E-240 (M.I. 22–28) and E-220 (M.I. 125–175) in Table V. It can also be seen that the greatest response to irradiation seems to be with copolymers with vinyl acetate content greater than 30 % as judged by gel content and by increase in the weight average molecular size of the soluble fraction. The effect upon the weight average molecular size, $\bar{A}_w$, in solution is also shown in Fig. 3. A plot of melt index *vs.* gel content (Fig. 4) shows that sample E-240 (27–29 % VA, 22–28 M.I.) produces the greatest degree of cross-linking for copolymers of the same composition. Samples with lower melt index (higher initial molecular weight) show less polymer growth. This is attributed to degradation of the polymer and is best illustrated by sample E-250 (27–29 % VA, 12–18 M.I.) in Table V which shows a decrease in gel content between 10.6 and 22.3 Mrad.

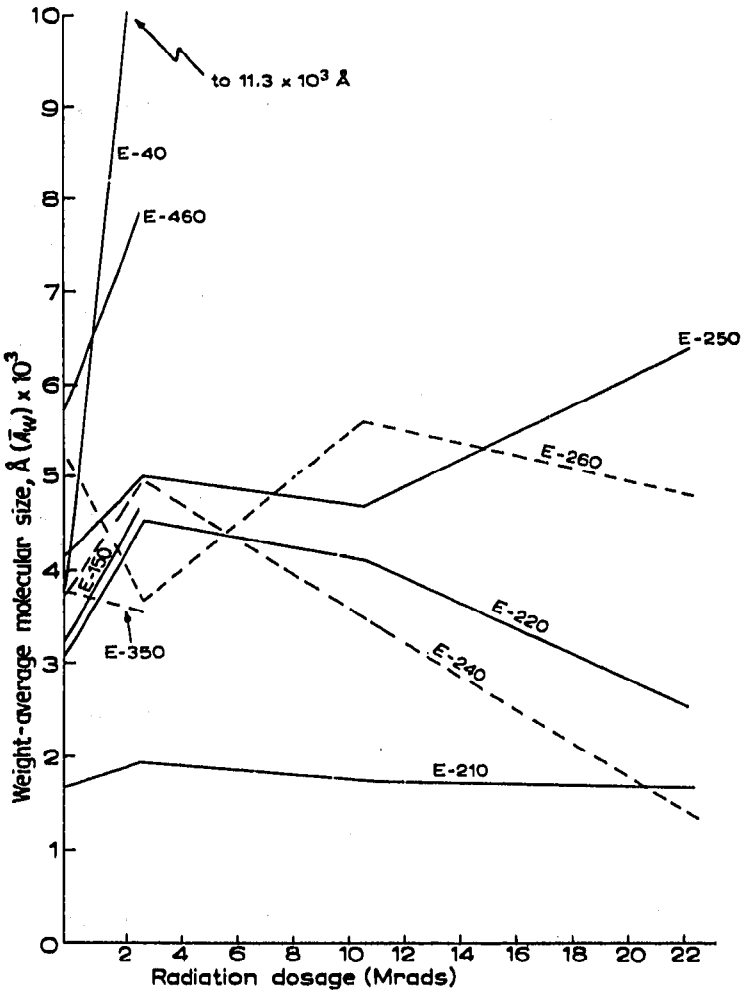

Fig. 3. Ethylene–vinyl acetate copolymers: molecular size *vs.* radiation dosage; *o*-dichlorobenzene solution.

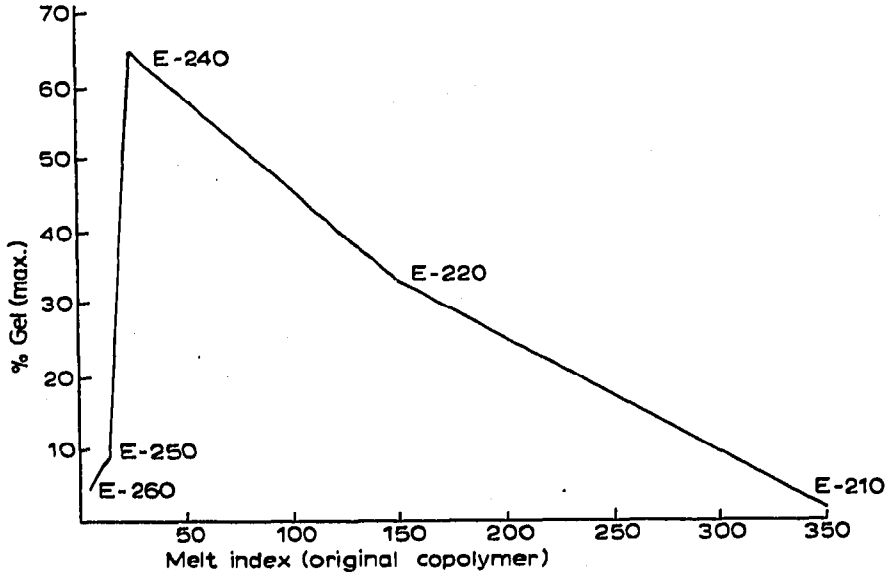

Fig. 4. Melt index *vs.* maximum gel content of ethylene–vinyl acetate copolymers containing 27–29% vinyl acetate.

TABLE VI

EFFECT OF γ-IRRADIATION ON MECHANICAL PROPERTIES

Ethylene–vinyl acetate copolymers: copolymers of varying molecular weight, same composition (28%, VA).

Sample No.	*M.I.* (*g/10 min*)	*Radiation dosage* (*Mrads*)	*Break stress* (*p.s.i.*)
E-210	340–370	0	511
		2.6	537
		10.6	582
		22.3	579
E-220	125–175	0	584
		2.6	1097
		10.6	1138
		22.3	1020
E-240	22–28	0	1179
		2.6	1245
		10.6	737
		22.3	2000
E-250	12–18	0	1371
		2.6	1312
		10.6	1395
		22.3	1122
E-260	5–7	0	2541
		2.6	2700
		10.6	2125
		22.3	1979

TABLE VII

EFFECT OF γ-IRRADIATION ON MECHANICAL PROPERTIES

Ethylene–vinyl acetate copolymers of similar molecular weight, varying composition.

Sample No.	*E/VA mole ratio*	*VA (%)*	*M.I. (g/10 min)*	*Radiation dosage (Mrads)*	*Break stress (p.s.i.)*	*Break elongation (%)*	*Tensile modulus (p.s.i. × 10^{-3})*
E-40	4.4/1	39–42	45–65	0	824	1247	0.35
				2.6	844	891	0.39
E-150	6.25/1	32–34	22–28	0	1026	1028	0.97
				2.6	917	698	0.95
E-240	8/1	27–29	22–28	0	1179	855	1.94
				2.6	1245	793	2.02
E-350	9.2/1	24–26	16–22	0	1679	921	2.80
				2.6	1755	836	2.72
E-460	14/1	17–19	2–3	0	2908	849	6.09
				2.6	3041	832	6.11

Samples E-250 and E-260, the higher molecular weight copolymers discussed above, showed significant losses in break stress (tensile strength) at 22.3 Mrad as shown in Table VI. Changes in breaking stress and tensile modulus were not significant at the 2.6 Mrad level for copolymers of similar molecular weight but varying composition (Table VII). However, the lessening in break elongation was significant except for sample E-460 (M.I. 2–3) which may have had little macro-Brownian movement to permit cross-linking due to the high molecular weight.

This study demonstrates that three parameters of radiation cross-linking of copolymers have been identified with molecular size distribution measurements conducted with GPC and gel content determinations. The three parameters are: (1) composition of copolymer, (2) molecular weight of starting material, and (3) radiation dosage. The cross-linking effect of each of these parameters can be deduced with these techniques which constitute a method for defining the optimum conditions for achieving a radiation cross-linked polymer. The validity of this approach is supported with measurements of physical properties which show correlation with the cross-linking effects observed with GPC and gel content studies.

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