Physical and Electrical Properties of Polyethylene Radiation Crosslinked via Polyfunctional Monomers

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Synopsis

The radiation crosslinking (via Co^{60}) of both high and low density polyethylene in the presence of several tetrafunctional monomers has been studied to observe the effects of the additives on mechanical and electrical properties. The monomers employed were allyl methacrylate, divinylbenzene, and diallyl maleate. Monomer levels were such that the number of moles present per number-average mole of polyethylene was 2.2-2.6 for AMA and DVB with Marlex 5003 and 6009, and 9-10 for Marlex 1712. The DAM level was 3-5% of that of the other monomers on the same basis. Gel fractions, tensile strengths (at yield and break) at ambient temperature and tensile strengths, elongations, and moduli measured at a temperature above which no crystallinity remains all undergo more marked changes in the presence of tetrafunctional monomer after only 1-3 Mrad of radiation, regardless of monomer nature. Gels, tensiles, and moduli increase while elongation decreases. The magnitude of the changes depends upon the monomer nature (at the above ratios), the order being AMA > DVB > DAM > Monomer-free. With increasing dose to 8 Mrad, the trends continue. The gel swelling ratios are inversely proportional to the $^3/_5$ power of the crosslink density, as determined by the modulus value in the absence of crystallinity. Straight radiation of monomer-free polyethylene to higher doses does not necessarily yield physical properties values attained at the lower doses with additive. The dielectric constant and dissipation factor of monomer-containing crosslinked polyethylene are only slightly affected by the presence of the polyfunctional monomer.

INTRODUCTION

The radiation crosslinking of low density polyethylene using polyfunctional monomers has previously been discussed.[1] In this paper, the process is extended to other types of polyethylenes with emphasis on a comparison of the efficiencies of various monomers in altering physical and dielectric properties in the low dose range. The polyfunctional monomer crosslinking process was studied in the range of 0–8 Mrad and compared with results obtained with doses up to 80 Mrad in the absence of the polyfunctional monomer. Co^{60} radiation was employed to attain doses up to 8 Mrad; higher doses were imparted by machine. The polymers

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employed were a typical high density polyethylene homopolymer, a low density homopolymer, and a high density polyethylene–polyisobutylene (5%) copolymer; monomers were divinylbenzene, diallyl maleate, and allyl methacrylate. The purpose of this work was to gain further insight into the property changes that result when radiation crosslinking is aided by polyfunctional monomers and to ascertain the limitations of this low dose crosslinking process.

EXPERIMENTAL

Materials

Polyethylene grades employed were Marlex 6009 ($\bar{M}_w$ = 1.2 × 10^5, $\bar{M}_n$ = 1.1 × 10^4), Marlex 5003 ($\bar{M}_w$ = 1.9–2.0 × 10^5, $\bar{M}_n$ = 0.93–1.1 × 10^4), and Marlex 1712 ($\bar{M}_w$ = 2.1 × 10^5, $\bar{M}_n$ = 2.8 × 10^4). Marlex 6009 is a high density (0.96 g./cc.) homopolymer, Marlex 5003 is a high density (0.95 g./cc.) copolymer with 5% butene-1, and Marlex 1712 is a low density (0.92 g./cc.) homopolymer. Marlex 1712 contains somewhat less than 0.1% 2,6-di-*tert*-butyl-*p*-cresol which acts as an antioxidant. Marlex 5003 and 6009 each contain an antioxidant mixture of the above cresol and dilauryl thiopropionate, the total not exceeding 0.1%. All polymers and molecular weight data were supplied by the Phillips Chemical Company. Polymer pellets were molded into 4$^1/_2$ × 2$^1/_2$ in. sheets of either 0.125 or 0.075 in. thickness, annealed at 90°C. for 5 hr. and slow-cooled prior to use. Monomers employed were allyl methacrylate (AMA), diallyl maleate (DAM), and divinylbenzene (DVB). The latter monomer is of 55–60% purity, the other components being ethylvinylbenzene and diethylbenzene. All monomers were used as received.

Polymer Treatment and Evaluation

Monomers were incorporated into the polymers by swelling as described earlier.[1] Co[60] radiations were performed in nitrogen to doses of 1, 3, 5, and 8 Mrad at 4 Mrad/hr. Machine irradiations were performed by placing samples on an aluminum tray which rested in a pan of Dry Ice that was passed under an electron beam generated by Model GS Van de Graaff accelerators. At 2 M.e.v., slabs 125 mil thick were irradiated at 2 Mrad/pass to 16, 32, 48, 64, and 80 Mrad; at 3 M.e.v., taped pairs of 125 mil slabs (i.e., 250 mil thick) were irradiated at 2 Mrad/pass to 11, 37, and 64 Mrad. Both sets of specimens were turned over after half the total number of passes required for these doses, the purpose being to attempt to attain a measure of uniformity in dose distribution. The dose variation that occurs throughout the specimen[2] was accounted for in the dose determination. An average variation of ±10% in the dose imparted to the irradiated specimen is calculated for the irradiation process.

Gel contents, swelling ratios of gels, and stress–strain measurements (using 3-in. standard dumbbells with gage length 0.876 in. and conforming to

ASTM D1708-59T) were performed as described earlier.[1] Tensile strength values at 25°C. were determined at yield and at break for high density polyethylene and at break for low density polyethylene. Tensile strength and elongation at break were also obtained at a temperature at which no crystallinity was present (135°C. for high density and 115°C. for low density polyethylene). Secant modulus at break, the ratio of stress at break to the total elongation, was calculated. Elevated temperatures were maintained by means of a constant temperature cabinet which allowed sample elongations to ca. 500%. Data for samples requiring greater elongations at break (some monomer-free samples, particularly in the 1–5 Mrad range) are not included. All monomer-containing samples broke under the test conditions. Samples were maintained at the specified temperature for 10–15 min. prior to testing.

Low temperature flexibility measurements of high density polyethylenes were determined via ASTM D 746-57T employing a Scott Model E impact testing machine. Test specimens were conditioned at room temperature for 48 hr. prior to the initiation of testing and maintained at the reduced temperature for 3 min. prior to being hit by the striking edge. With five or six samples being tested simultaneously, the striking edge was observed to move at 6–9 ft./sec. Breakage was sharp on occasion, but many specimens had to be evaluated by bending and examination after the guillotine had struck. An average of 24 specimens was employed to obtain each experimental point. Cooling during testing was maintained by employing isopentane–Dry Ice mixtures. The brittle point (T_b) was determined by plotting the probability of failure versus the temperature of testing.

Measurements of dielectric constant and dissipation factor were performed on disk specimens which were 1–2 in. in diameter and approximately 0.1 in. thick. Gold electrodes were evaporated onto the specimens. Measurements were made using a micrometer–electrode system as described in ASTM D 150-59T. For measurements at 1 kcycle/sec., a modified Shering bridge was employed, and at 1 Mcycle/sec., a Q-meter was employed.

RESULTS AND DISCUSSION

Polymer Swelling by Monomer

The results obtained upon swelling the three polyethylene polymers in the monomers to equilibrium are shown in Table I.

It is seen that the low density polymer contains about $1/3$ more of the aromatic or monoester monomer than does the high density polymer, and that the diester monomer is barely incorporated into any of the polyethylenes. Since the divinylbenzene is about 50% pure, the molar tetrafunctional contents of the polyethylene–DVB systems are about equal to those of the polyethylene–AMA systems.

The molar ratio of tetrafunctional monomer to polyethylene was calculated by dividing the mole per cent monomer present (number of moles of

TABLE I
Equilibrium Swelling of Polyethylene by Tetrafunctional Monomer

| | Polyethylene grade | | | | | |
| | Marlex 5003 | | Marlex 6009 | | Marlex 1712 | |
Monomer	Wt. %	Moles/no. avg moles PE	Wt. %	Moles/no. avg moles PE	Wt. %	Moles/no. avg moles PE
AMA	2.9	2.2	2.9	2.5	4.0	9.0
DVB	6.3	2.3	6.3	2.6	9.8	10
DAM	0.10	0.10	0.15	0.12	0.30	0.28

monomer in 100 g. polyethylene) by the number-average moles of poly-ethylene present (100 g./$\bar{M}_n$).   It is seen that the double bond content of tetrafunctional monomer per mole of polyethylene is similar for the two high density polyethylenes if AMA or DVB is the monomer under consideration (although the latter does contain a quantity of ethylvinyl-benzene).   On this basis, the low density polyethylene contains about four times as much monomer as the high density polyethylene.   The molar ratio of DAM to polyethylene is ca. 1/20–1/30 that of the other monomers to polyethylene, and is 2–3 times greater in the low density polyethylene than in the high density polyethylenes.

Gel-Dose Studies

The gel fraction resulting from the radiation of polyethylene can be employed as a guide to the changes that result.[3,4]   The ability of these three polyfunctional monomers to reduce the incipient gelation dose (the minimum dose required to yield insoluble gel) for these polyethylene grades is depicted in Figure 1; it can also be seen that the presence of monomer yields a higher gel fraction at any dose level than would be the case for the monomer-free polyethylene irradiated to the same dose. The observed order of efficiency is AMA > DVB > DAM > monomer-
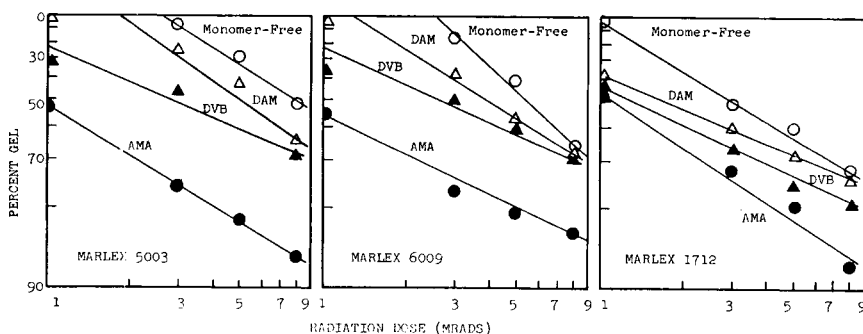

Fig. 1. Per cent gel vs. radiation dose for Marlex 5003, Marlex 6009, and Marlex 1712. Dose of 1–8 Mrad in presence of polyfunctional monomer.

free. For each grade, a dose of 8 Mrad in the presence of AMA gives 85% gel or greater, as compared with only 45–70% gel which results from the same exposure of monomer-free polyethylene. Figure 1 also confirms that the incipient gelation dose is reduced regardless of the monomer nature.

Incipient gelation doses were determined for the three monomer-free polyethylenes by extrapolation to 100% sol of their curves of gelation versus machine radiation dose. These incipient gelation doses were used to calculate $G_{crosslink}$ values of 1.3–1.5 for the three polyethylene grades. The $G_{crosslink}$ value is the number of crosslinks resulting from the absorpton of 100 e.v. of radiation. The $G_{crosslink}$ value of monomer-containing polyethylene, determined by this same method,[1] is considerably higher than that of monomer-free polyethylene.

Tensity Strength Properties at Ambient Temperature

The effect of radiation on the tensile strength of low density polyethylene has been discussed by Charlesby[3,5] and Lawton.[6] With increasing dose,
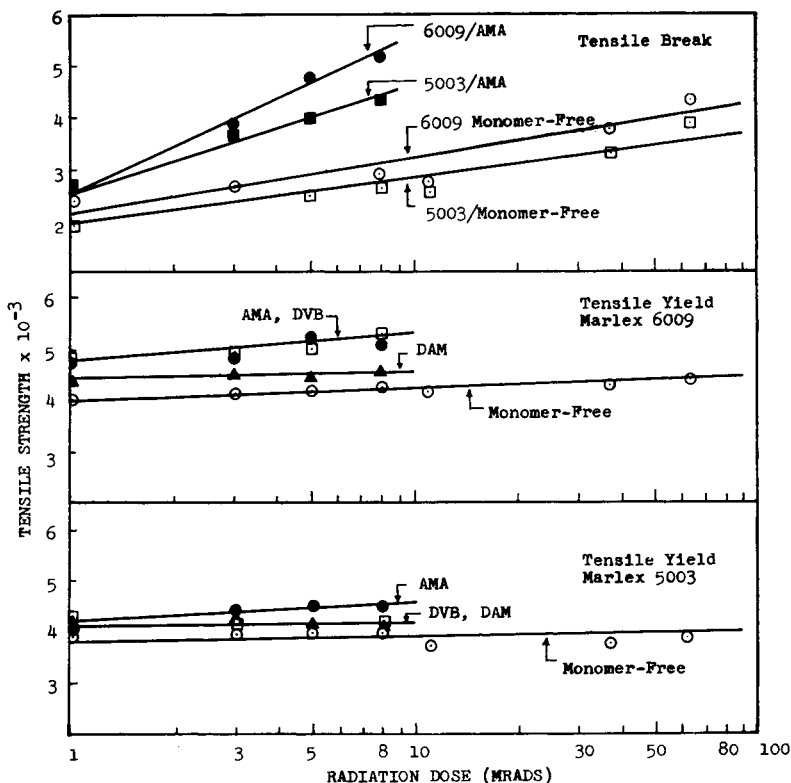

Fig. 2. Tensile strength vs. radiation dose for high density polyethylene irradiated in presence of allyl methacrylate, divinylbenzene, diallyl maleate, and no additive; measurement at 25°C.

the tensile strength reached a maximum and then decreased. Wright[7] has reported that radiation of various high density polyethylenes caused an increase in yield stress with doses up to 75 Mrad.   The increases, however, were only about 200–500 psi (or 5–12% of the values for the unirradiated polyethylene).   Ultimate tensile strength also increased, although results were more complex at lower doses.   It has been further observed that the irradiation of low density polyethylene to 10 Mrad or more in the presence of allyl methacrylate increased its tensile strength by about 25%.[1]

Figure 2 shows the effect of radiation on the tensile at yield and at break for the two high density polyethylenes, both in the presence and absence of tetrafunctional monomer.   It will be observed that both high density grades undergo an increase in tensile at yield as the dose becomes greater, the improvement being more marked when tetrafunctional monomer is present.   In the latter case, after only 1 Mrad of radiation, the tensile strength increases by 10–20% (from 3600 psi for unirradiated Marlex 5003 and 4000 psi for unirradiated Marlex 6009) and, after 8 Mrad, further slight tensile increases are obtained; tensile yield values at the latter dosage exceeded 5000 psi.   Of great significance is the fact that the monomer-free systems (irradiated to 8 Mrad via Co^{60} and to 11–64 Mrad via machine) never attain the tensile strengths exhibited by the monomer-containing systems.   The tetrafunctional monomers differ in their efficiencies, the order being AMA > DVB > DAM.   This is the same order of efficiency observed in the gelation study.

Figure 2 also indicates how the tensile strength at break varies with radiation dose both in the presence and absence of allyl methacrylate. Straight radiation (i.e., without monomer) of Marlex 6009 causes an increase to 4000–4400 psi after ca. 64 Mrad.   With AMA present, the ultimate tensile strength is greater than 5000 psi after only 8 Mrad.   Here also, the tensile strength attained in the presence of the monomer is never attained in the absence of the monomer.   The ultimate tensile strength improvement for irradiated low density Marlex 1712 containing monomer in the 1–8 Mrad range is less than in the case of the high density polyethylenes.

These results clearly indicate that the tensile strength of high density polyethylene can be enhanced by small quantities of tetrafunctional monomers coupled with irradiation to low doses (<8 Mrad).   Both the tensile at yield and at break are increased to a greater extent than occurs upon straight radiation to considerably higher doses.

A reduction in the monomer level by $1/3$ to $1/2$ in the high density grades was found to have no significant effect on the tensile behavior after 1–3 Mrad.

Tensile Strength Properties Above T_m

The tensile strength of polyethylene decreases with increasing temperature.   As the temperature is raised, crystalline melting occurs; the

polymer chains slide past each other more easily, and the tensile strength decreases. Above the melting temperature T_m, i.e., where all of the crystallinity has disappeared, polyethylene exhibits zero tensile strength. Irradiated polyethylene, however, behaves like a crosslinked elastomer above the normal polymer T_m; it remains coherent, and the tensile strength, although very low, can be measured. The tensile strength below T_m is due
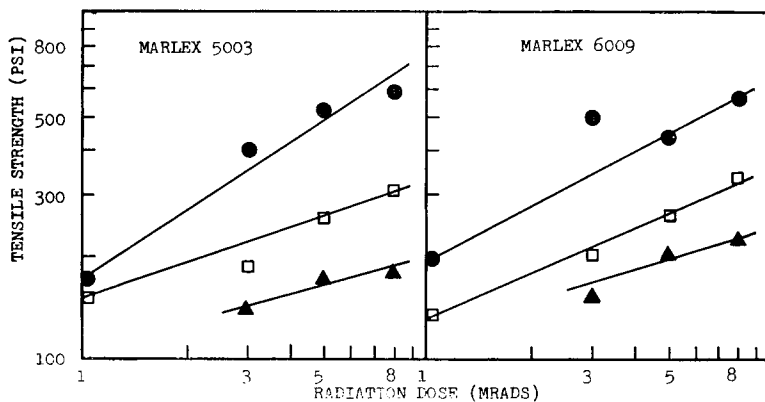
Fig. 3. Tensile strength vs. radiation dose for high density polyethylene at 135°C. in presence of (●) allyl methacrylate, (□) divinylbenzene, and (▲) diallyl maleate.
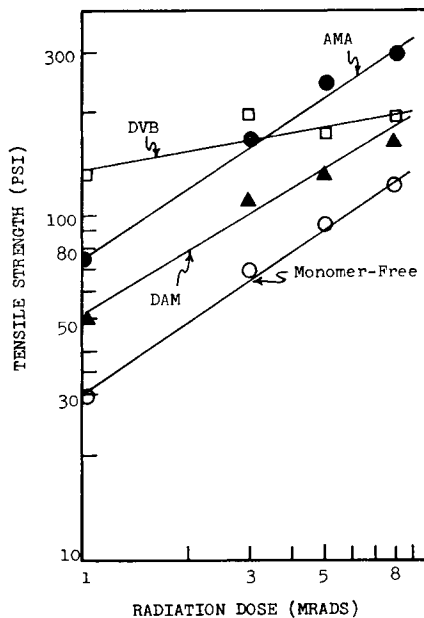
Fig. 4. Tensile strength vs. radiation dose for low density Marlex 1712 polyethylene at 115°C. in presence of (●) allyl methacrylate, (□) divinylbenzene, (▲) diallyl maleate, and (○) no additive.

to both the polymer crystallinity and the degree of crosslinking, while above T_m it is due solely to the latter.

Figures 3 and 4 show the results obtained upon tensile testing at temperatures above which the polyethylenes would melt if they were unirradiated (noncrosslinked). Figure 3 indicates that all the monomer-containing high density polyethylene systems increase in tensile strength with dose over the 1–8 Mrad range; values of 500–600 psi are obtained for Marlex 5003 and 6009 with allyl methacrylate. The other two monomers promote sufficient crosslinking that tensile strengths of over 150 psi are developed at these low doses. The monomer-free high density polyethylenes irradiated to the same doses exhibit elongations of greater than 500% and do not break under the test conditions; presumably they are not sufficiently crosslinked to offer appreciable tensile strengths. The monomer-free specimens irradiated to higher doses (11–80 Mrad) exhibit tensile strengths of 150–200 psi. These latter samples are therefore comparable in this regard to the 1 Mrad specimens containing allyl methacrylate or divinylbenzene, or the 3–8 Mrad specimens containing diallyl maleate. The higher doses in the absence of monomer do not allow Marlex 5003 and 6009 to exhibit the same tensile strength as the monomer-containing systems. Figure 4 indicates the monomer efficiencies in the Marlex 1712 systems. Tensile strengths as high as 300 psi are obtained for the AMA system receiving 8 Mrad. All the monomer-containing systems exhibit higher tensile strength than the monomer-free controls at equivalent doses. Thus, under conditions where polyethylene crystallinity cannot contribute to the tensile strength, the utility of the polyfunctional monomer in the 1–8 Mrad range is observed. It is clear that the tensile strength, in the absence of any effects due to polymer crystallinity, is enhanced by the tetrafunctional monomer crosslinking process. The effects are significant in this low dose range.

A reduction in the monomer (AMA or DVB) level by $^1/_3$ to $^1/_2$ causes a decrease in tensile strength of high density polyethylene at 135°C. where crystallinity is absent.

The elongations at break of high density, monomer-containing systems at 135°C. are sharply reduced in the 1–8 Mrad range, as compared to monomer-free systems at the same doses. In the 3–8 Mrad range, the AMA systems exhibit the lowest elongations (100–150%). Monomer-free systems irradiated to 50–80 Mrad exhibit elongations of 50–100%, the values being over 400–500% at doses of 8 Mrad or less.

Modulus

The secant moduli at break for the systems tested at the elevated temperatures (135°C. for high density polyethylene and 115°C. for low density polymer) are shown in Figure 5 and 6. It can be seen that the modulus of both monomer-free and monomer-containing polyethylene measured under these conditions increased with dose; however, the monomer-containing systems yield higher moduli after equivalent doses. Straight
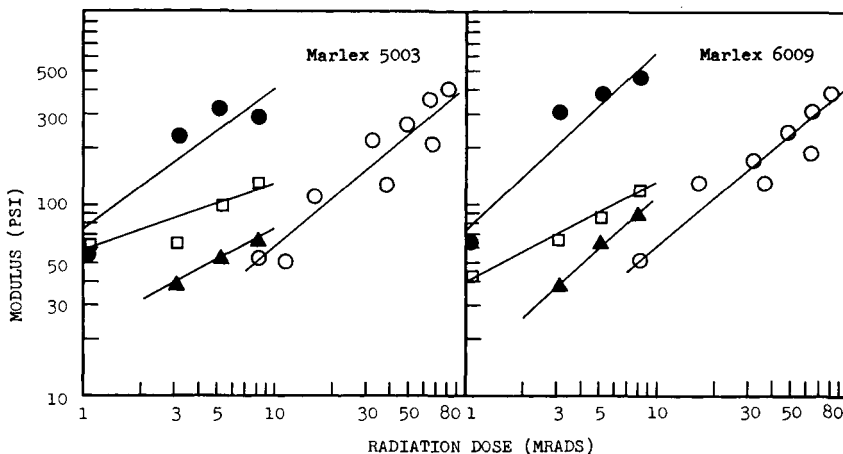
Fig. 5. Modulus at 135°C. vs. dose for high density polyethylenes irradiated in presence of (●) allyl methacrylate, (□) divinylbenzene, and (▲) diallyl maleate; (O) monomer-free irradiations, Co[60] and machine.
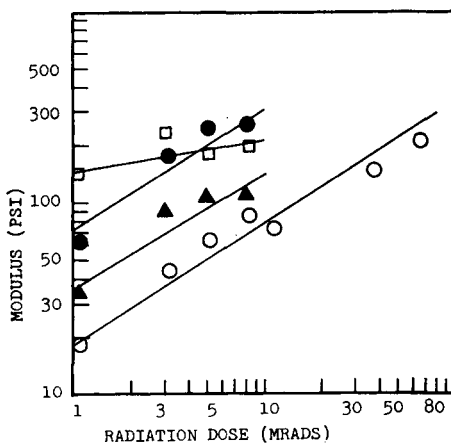

Fig. 6. Modulus at 115°C. vs. dose for low density Marlex 1712 irradiated in presence of (●) allyl methacrylate, (□) divinylbenzene, and (▲) diallyl maleate; (O) monomer-free irradiations, Co[60] and machine.

radiation to ca. 64 Mrad results in moduli of 200–300 psi for all grades; with 8 Mrad moduli are 50–70 psi. When AMA is present, irradiation to 8 Mrad yields moduli between 200 and 500 psi.

Correlation of Modulus and Tensile Strength above T_m with Gel Fraction Swelling Ratios

Since the modulus and tensile strength of crosslinked polyethylene at a temperature above which no crystallinity remains represents a measurement upon a rubbery material, these parameters can be correlated with others dependent upon rubbery behavior. The gel fraction equilibrium swelling
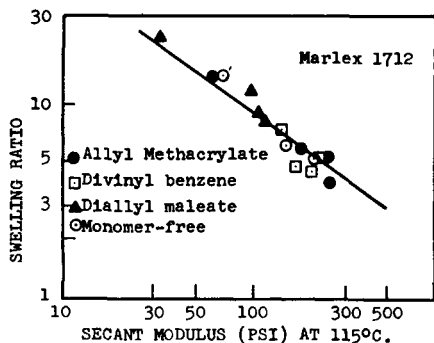
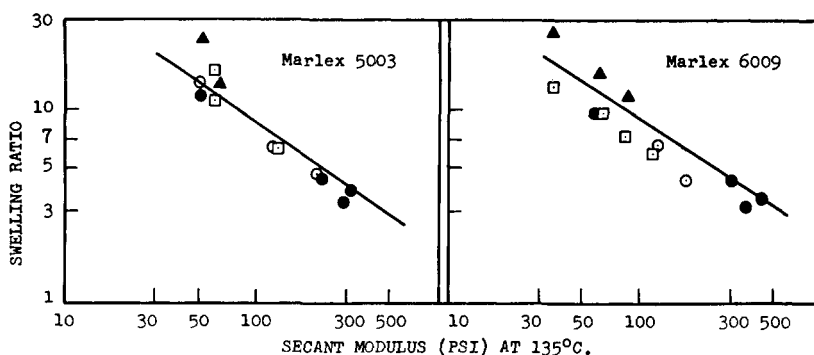Fig. 7.   Modulus at 115°C. vs. gel swelling ratio for irradiated Marlex 1712.

Fig. 8. Moduli at 135°C. vs. gel swelling ratio for irradiated Marlex 5003 and 6009.

ratio q_m represents such a parameter, since it is obtained under the comparable conditions of absence of crystallinity.   Swelling ratios are related to the molecular weight between crosslinks M_c for rubbery elastomers[8] and correlation of both modulus and tensile strength with M_c has been discussed by Flory[9] for crosslinked natural rubber.   Correlation has also been discussed for styrene–butadiene (SBR) rubber,[10] and these results have been evaluated by Bueche.[11]   Flory's data[9] show that the swelling ratio is inversely proportional to the 3/5 power of the crosslink density, the latter being determined by measuring the 300% modulus of the rubber. Charlesby[3] has shown that, with polyethylene, swelling ratio can be correlated with radiation dose in place of modulus; the two are proportional to each other.   It has been previously shown that the use of polyfunctional monomer to aid the radiation crosslinking of polyethylene offers the same radiation dose–swelling ratio relationship but at reduced doses.[1]   This information made it appear likely that the swelling ratios of all the cross-linked systems could be correlated with their elevated temperature moduli. Figures 7 and 8 depict the modulus–swelling ratio relationships.   It is seen that these polyethylene systems behave in a similar fashion to Flory's rubber specimens.   For all polyethylene (high dose) and polyethylene–multifunctional monomer (low dose) systems, linear log-log plots are

obtained with slopes of $-3/5$, with monomer nature not being a factor. This occurs because the crosslink densities of the polyethylenes fall within the same range regardless of the dose differences between the monomer-free and monomer-containing systems. It is seen, therefore, that crosslinked polyethylene–multifunctional monomer moduli above T_m can be correlated with q_m or M_c in a similar fashion to crosslinked rubber.

Low Temperature Flexibility

Low temperature flexibility (or brittleness) of polyethylene has been discussed by Sandiford and Willbourn.[12] In general, flexibility is aided by high molecular weight, high density, and low polydispersity. It has been suggested that the lower limiting value of the brittle temperature (T_b) is associated with the $-120°$C. transition of the amorphous regions. Figure 9 shows the effect of radiation on the T_b of Marlex 5003 and 6009. Both unirradiated polymers exhibit brittle points in the -114 to $-117°$C. range; radiation raises the T_b, although Marlex 5003 appears to be slightly more flexible at lower doses. Similar results of the same order of magnitude were obtained when Marlex 5003 or 6009 was irradiated in the presence of AMA. In view of the inherent limitations of this test,[13,14] including the varied effect of sample preparation, comparison with prior work is not feasible.
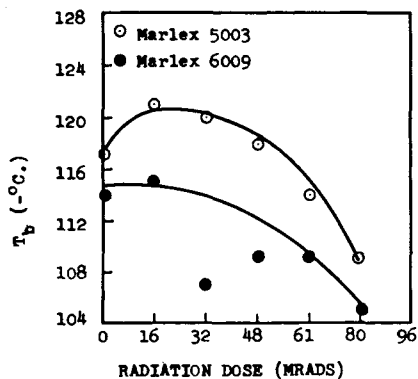

Fig. 9. Brittleness temperature T_b vs. radiation dose for Marlex 5003 and 6009.

Dielectric Properties

Dielectric measurements (dielectric constant and dissipation factor) for polyethylene specimens are summarized in Table II. The data cover the following systems: (a) monomer-free and monomer-containing Marlex 1712, 5003, and 6009 irradiated to 1–8 Mrad via Co[60] in nitrogen; and (b) monomer-free systems irradiated via machine in air to 11–37 Mrads.

It should be noted that the machine-irradiated samples were large enough to allow for the fabrication of 2-in. diameter dielectric specimens, whereas Co[60]-irradiated samples were smaller and restricted the dielectric

TABLE II
Dielectric Properties of Irradiated Polyethylenes

Poly-ethylene type	Radiation range		Dielectric constant (K) range		Dissipation factor (tan δ) range		Monomer nature
	Dose, Mrad	Source	1 kcycle	1 Mcycle	1 kcycle	1 Mcycle	
Marlex 5003	0–37	Machine	2.33–2.37	2.33–2.36	0.0001	0.0001	None
	1–8	Co⁶⁰	2.32–2.33	2.32–2.35	0.0004	0.0004	None
	1–8	Co⁶⁰	2.31–2.35	2.33–2.35	0.0004	0.0004–0.0005	AMA
	1–8	Co⁶⁰	2.33–2.35	2.35–2.37	0.0003–0.0004	0.0005	DVB
	1–8	Co⁶⁰	2.31–2.34	2.33–2.35	0.0004	0.0005	DAM
Marlex 6009	0–37	Machine	2.34–2.39	2.33–2.40	0.0001	0.0001	None
	1–8	Co⁶⁰	2.34–2.35	2.34–2.35	0.0002–0.0003	0.0004–0.0007	None
	1–8	Co⁶⁰	2.34–2.37	2.33–2.38	0.0003–0.0009	0.0004–0.0008	AMA
	1–8	Co⁶⁰	2.35–2.37	2.36–2.38	0.0002–0.0003	0.0004–0.0007	DVB
	1–8	Co⁶⁰	2.34–2.38	2.33–2.36	0.0003–0.0004	0.0004	DAM
Marlex 1712	0–37	Machine	2.27–2.28	2.27–2.29	0.0001	0.0001	None
	1–8	Co⁶⁰	2.29–2.31	2.28–2.30	0.0003	0.0004	None
	1–8	Co⁶⁰	2.27–2.30	2.26–2.33	0.0007–0.0018	0.0005–0.0009	AMA
	1–8	Co⁶⁰	2.27–2.33	2.27–2.33	0.0003	0.0004	DVB
	1–8	Co⁶⁰	2.28–2.32	2.27–2.30	0.0004	0.0004	DAM

specimens to ca. 1 in. in diameter. This distinction resulted in a difference in the limit of precision of measurement. For example, the limit of measurement of tan δ of a 2-in. specimen is about 0.0001, whereas that for a 1-in. specimen is of the order of 0.0004. Consequently, it should not be concluded from the tables of data that Co^{60} irradiation results in greater dielectric losses than machine irradiation at the same dose level.

In comparing the 1–8 Mrad Co^{60} systems irradiated in nitrogen in the presence and absence of monomer, it is seen that the monomer has a negligible effect on the dielectric constant K and a small effect on the dissipation factor; this latter effect is most pronounced where allyl methacrylate, the most polar of the monomers, was employed.

The machine-treated polyethylene systems show that straight radiation has a negligible effect under these conditions of air irradiation. Changes in K or tan δ are not observable to a dose of 37 Mrad. There is some indication that doses above 48 Mrad in air cause increases in tan δ, due possibly to oxidation.

CONCLUSIONS

Co^{60} radiation of typical high and low density polyethylenes (Marlex 5003, 6009, and 1712) in the presence of allyl methacrylate, divinylbenzene or diallyl maleate induces more marked physical property changes than does straight radiation in the absence of monomer. The changes result from increased crosslinking at low doses due to the additive. The changes due to the polyfunctional monomer presence may be summarized as follows: (a) Increased tensile strength at yield and at break occur after only 1 Mrad. The tensile at break increases with dose to 8 Mrad. Without monomer, even 80 Mrad is insufficient to reach the 8 Mrad/monomer tensile strength. (b) Increased tensile strength and modulus occur in the 1–8 Mrad range at elevated temperatures wherein the polymer is completely void of crystallinity; tensile strengths of ca. 600 psi are obtained after 8 Mrads. (c) Reduced elongations occur at doses in the 1–8 Mrad range when polyfunctional monomer is present.

The moduli of irradiated monomer-free and monomer-containing polyethylenes, as measured at an elevated temperature at which no crystallinity is present, are inversely proportional to the swelling ratios of the gel fractions; this behavior is typical of crosslinked rubbers. Both modulus and swelling ratio are measures of the crosslink density. Monomer nature is not a factor in the 1–8 Mrad range. All polyfunctional monomer-crosslinked systems exhibit this behavior.

The crosslinking process is aided to the greatest extent by allyl methacrylate; only 2.2–2.6 moles/number-average mole of Marlex 5003 or 6009 are required. Divinylbenzene at the same level is only slightly less efficient, and diallyl maleate at 0.10–0.15 mole-% is still better than the monomer-free system. On this basis, low density Marlex 1712 contains 2 to 4 times as much monomer as the high density polymer.

Machine irradiation to 80 Mrad offers gel fractions and high temperature moduli essentially comparable to 8 Mrad systems containing AMA; however tensile strengths are not as high as those exhibited by the monomer-containing system.

Dielectric properties, i.e., dielectric constant and dissipation factor, are only slightly altered by the presence of monomer. The polyfunctional monomer technique for facilitating radiation crosslinking is therefore of potential utility for dielectric applications.

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Résumé

Le pontage par radiation au Co⁶⁰ de polyéthylène de haute et de basse densité en présence de monomères tétrafonctionnels a été étudié en vue d'observer les effets de ces additifs sur les propriétés mécaniques et électriques. Les monomères utilisés étaient le méthacrylate d'allyle, le divinyl benzène et le maléate de diallyle. Les quantités des monomère étaient telles que le nombre de moles présentés par molécules moyenne de polyéthylène était de 2.2 à 2.6 pour AMA et DVB dans le cas du Marlex 5003 et 6009 et 9 à 10 pour le Marlex 1712. La quantité de DAM était de 3 à 5% de celle des autres monomères sur la même base. Les fractions de gel, les forces à la tension (rendement, et à la cassure) à température ambiante, les forces à la traction, les élongations et les modules mesurés à une température supérieure à celle où disparait toute cristallinité, tous subissent des modifications plus ou moins marquées en présence du monomère tétrafonctionnel lorsque uniquement 1 à 3 Mrd de radiation ont été utilisées, indépendamment de la nature du monomère. Les gels, les tensions, et les modules croissent lorsque l'élongation décroît. L'importance des modifications dépend de la nature du monomère (au rapport cidessus), l'ordre étant MA > DVB > DAM > absence du monomère. En accroissant la dose jusque 8 Mrad, les modifications continuent, les rapports de gonflements de gel sont inversément proportionnels à la puissance ³/₅ de la densité de pontage ainsi que cela a été déterminé par la valeur du module en absence de cristallinité. L'irradiation directe du polyéthylène en absence de cristallinité. L'irradiation directe du polyéthylène en absence de monomère à des doses élevées ne fournit pas nécessairement des propriétés physiques obtenables à plus faibles doses en présence d'additifs. La constante diélec-

trique et le facteur de dissipation du polyéthylène ponté contenant du monomère sont uniquement faiblement affectés par la présence de monomères polyfonctionnels.

Zusammenfassung

Die Strahlungsvernetzung (durch Co⁶⁰) von Polyäthylen hoher und niedriger Dichte in Gegenwart einiger tetrafunktioneller Monomerer wurde zur Ermittlung des Einflusses der Additive auf die mechanischen und elektrischen Eigenschaften untersucht. Als Monomere wurden Allylmethacrylat, Divinylbenzol und Diallylmaleat verwendet. Die Molzahl des Monomeren pro Zahlenmittelmol Polyäthylen betrug für AMA und DVB bei Marlex 5003 und 6009 2,2 bis 2,6 und bei Marlex 1712 9 bis 10. Die DAM-Konzentration betrug 3–5% derjenigen der anderen Monomeren auf die gleiche Basis bezogen. Gelbruchteil, Zugfestigkeit (be der Elastizitäts- und Bruchgrenze) bei Raumtemperatur und Zugfestigkeit, Dehnung und Modul bei einer Temperatur, oberhalb derer keine Kristallinität zurückbleibt, alle diese Eigenschaften erfahren stärker ausgeprägte Änderungen in Gegewart eines tetrafunktionellen Polymeren nach einer Bestrahlung von 1–3 Mrad, unabhängig von der Natur des Monomeren. Gelbruchteil, Zugfestigtike und Modul nehmen zu, während die Dehnung abnimmt. Die Grösse der Änderung hängt von der Natur des Monomeren ab (bei den oben angegebenen Verhältnissen); die Reihenfolge ist AMA > DVB > DAM > ohne Zusatz. Bei Erhöhung der Dosis bis zu 8 Mrad bleibt das Verhalten das gleiche. Der Quellungsgrad des Gels ist der ³/₅-Potenz der durch den Wert des Moduls in Abwesenheit bei fehlender Kristallinität bestimmten Vernetzungsdichte umgekehrt proportional Eine Bestrahlung von monomerfreiem Polyäthylen mit höheren Dosen führt nicht notwendig zu Werten der physikalischen Eigenschaften, welche bei niedrigeren Dosen mit Additiv erreicht werden. Die Dielektrizitätskonstante und der Dissipationsfaktor von monomerhältigem vernetzen Polyäthylen werden durch die Gegenwart des polyfunktionellen Monomeren nur wenig beeinflusst.