

Radiation-Crosslinked Polypropylene: Physical and Dielectric Properties

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Synopsis

Irradiation of two stereoregular polypropylenes and a polyallomer via ^{60}Co in the presence of 3–8% allyl methacrylate (AMA) monomer, to doses up to 5 Mrad, lead to an improvement in mechanical properties. With irradiation, heat resistance, tensile strength, and gel fractions increased, and creep compliance decreased. The decrease in creep compliance was revealed by measurements of irradiated samples at 185°C (at constant load and monomer level), a temperature above the T_m of polypropylene. Dielectric properties (dielectric constant K and dissipation factor $\tan \delta$) were virtually unaffected by irradiation of 0.3 to 5.0 Mrad in nitrogen when AMA was absent. In the presence of monomer, small but generally tolerable increases in $\tan \delta$ resulted if the monomer concentration was not too great. To obtain improvements in mechanical properties while not simultaneously altering the dielectric losses, it was necessary to keep the AMA concentration to a maximum of 4%.

INTRODUCTION

The effect of high-energy radiation on polypropylene has been discussed in a number of publications over the past several years.^{1–4} The polymer simultaneously crosslinks and degrades with irradiation, and the extent of each process, other factors being equal, is apparently dependent upon the degree of crystallinity. Stereoregular polypropylene crosslinks less efficiently than does polyethylene. The kinetics and possible mechanisms of crosslinking, degradation, gas evolution, and other effects of irradiation of the hydrocarbon polymer have been reviewed and discussed by Dole.⁵ The incorporation of allyl methacrylate (AMA) monomer into polypropylene prior to irradiation facilitates crosslinking of the polymer, as it does with polyethylene.^{6,7} This paper discusses the changes in physical and dielectric properties that result from γ -irradiation of two polypropylene-AMA systems and one polyallomer-AMA system.

EXPERIMENTAL

Polypropylene grades employed were Tenite 4221 and Tenite 4D31; the ethylene-propylene copolymer was Tenite polyallomer 5C21. Tenite

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4221 is an unmodified polypropylene, while Tenite 4D31 contains approximately 30% polyisobutylene (to aid low-temperature flexibility). All polypropylenes were supplied by Tennessee Eastman Company; molecular weight information on these materials is not available. Allyl methacrylate monomer was supplied by Sartomer Resins, Inc., and used as received. Polymer sheets having dimensions $4\frac{1}{2}$ in. length \times $2\frac{1}{2}$ in. width \times 0.125 in. thickness were obtained by injection molding; sheets were annealed 5 hr at 90°C and slow-cooled prior to use. Monomer was incorporated into the polymers via swelling.⁶ ^{60}Co irradiations were performed under nitrogen to doses of 0.3, 1.0, 3.0, and 5.0 Mrad at 0.02–0.05 Mrad/hr with the use of the RAI source; all γ -irradiated specimens were dried *in vacuo* for 18 hr at 90°C prior to being evaluated. Machine irradiations were performed to impart uniform doses⁷ of 5.3, 16.0, 26.7, and 37.3 Mrad by employing a High Voltage Engineering Corp., 2-MeV Model GS Van de Graaff accelerator at 2 Mrad/pass.⁶ Machine irradiations were performed directly upon the $4\frac{1}{2}$ -in. slabs, and dumbbell-shaped specimens used in measuring mechanical properties were cut afterwards. ^{60}Co irradiations were performed on dumbbell-shaped specimens. All disks for dielectric testing were prepared subsequent to irradiation.

Gel fractions, stress-strain measurements, and dielectric measurements were performed as described earlier.^{6,7}

Creep measurements at elevated temperatures (145 and 185°C) were performed by clamping dumbbell specimens at both ends of the gage length (0.876 in.), placing the clamped specimen into a Missimers constant-temperature heating cabinet, attaching a load to the specimen, via a copper wire, through the bottom of the cabinet, and following the length increase with time by means of a cathetometer. The loads on the specimens were as follows: 145°C , Tenite 4D31, 10.4 psi; 185°C , Tenite 4D31, 7.4 psi; 185°C , Tenite 4221, 7.9 psi; 185°C , Tenite 5C21, 8.0 psi. After the 2 min allowed for each specimen to come to equilibrium with its environment, the increase in length was determined every 30–60 sec; after 5 minutes, readings were taken less often. Four to six identical specimens were tested for each dose, and creep compliance was plotted against time.⁸ The com-

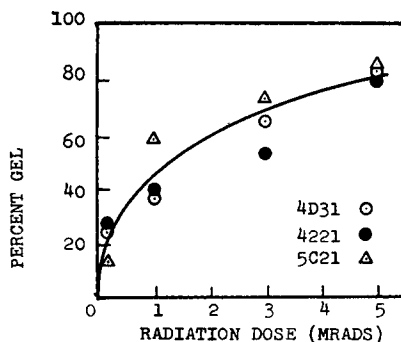


Fig. 1. Gel vs. dose for polypropylene-AMA systems.

bined data were then employed to obtain a master curve which represents the average behavior of the polypropylene specimens containing a specific quantity of AMA and irradiated to a specific dose. 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 by using a micrometer-electrode system as described in ASTM D 150–59T. For measurements at 1 kHz, a modified Shering bridge was employed, and at 1 MHz, a Q-meter was employed.

RESULTS AND DISCUSSION

Monomer Incorporation and Gel Fractions

All three polypropylene grades exhibited a small weight gain upon swelling in allyl methacrylate (AMA) monomer. After γ irradiation of 0.3–5.0 Mrad and vacuum drying to remove unreacted monomer, a net or retained weight gain of $6.5 \pm 1\%$ for Tenite 4D31 and 5C21, and $3.4 \pm 0.7\%$ for Tenite 4221 resulted.

The relationship of gel fraction to dose for these systems is shown in Figure 1. Gel fractions were obtained at the lowest dose employed (0.3 Mrad) and increased with dose. All three systems exhibited over 80% gel after irradiation to 5 Mrad. Irradiation of polypropylene in the absence of monomer does not generally lead to the formation of a gel fraction unless very high doses are employed, since the polymer simultaneously degrades almost as fast as it crosslinks.⁹ In this study, irradiation (0.3–5.0 Mrads) of polypropylene alone under conditions identical to those employed with the monomer-containing systems, failed to yield any detectable gel fraction. As seen in Figure 1, incorporation of AMA into the polymer prior to the irradiation allowed crosslinking and gel formation to proceed.

None of the monomer-free systems machine-irradiated to 5.3–37 Mrad exhibited gel fractions except the polyallomer, which gelled to the extent of 33% when irradiated to 37 Mrad. The behavior of this polymer after irradiation can be expected to be halfway between that of polyethylene and polypropylene: a 50/50 ethylene-propylene copolymer has been reported to exhibit a $G_{\text{scission/crosslinking}}$ equivalent to that of polyethylene.¹⁰ This gel study demonstrated that the polypropylene and polyallomer hydrocarbon polymers could, upon monomer incorporation, be induced to crosslink efficiently via radiation and yield high gel fractions. The mechanism of the monomer-induced radiation crosslinking reaction has been discussed for low-density polyethylene in a previous publication,⁶ and it is reasonable to assume it applicable for the hydrocarbon polymers employed herein.

Tensile Strength and Elongation at Room Temperature

The relationship of tensile strength and radiation dose is shown in Figures 2 and 3. Figure 2 indicates the results for straight irradiation via machine

and covers doses to 37 Mrad. The tensile strength of the polypropylene-polyisobutylene blend, Tenite 4D31, decreased with dose (2800 psi to 2000 psi); the tensile strength of the unmodified polypropylene Tenite 4221, underwent an initial increase (4800 to 5800 psi after 5 Mrad) and then decreased significantly with increasing dose; the tensile strength of the 5C21 polyallomer remained essentially constant with dose. For all three polymers, significant improvement in tensile strength was either minor or did not occur at all. Figure 3 indicates the results for the samples irradiated after swelling with AMA monomer prior to ^{60}Co irradiation. These data cover a considerably smaller dose range (to only 5 Mrad); yet improvements in tensile strength are readily apparent. The improvements in tensile strength for these three polypropylenes in the presence AMA paralleled the results obtained with polyethylene^{6,7} and probably are attributable to enhanced, radiation-induced crosslinking.

A decrease in elongation occurred upon irradiation, regardless of whether AMA was present or absent, although the effect was more pronounced with AMA present. This is shown in Figure 4 (note change in dose scale).

High-Temperature Creep Studies

High temperature creep measurements were performed on the ^{60}Co -irradiated polypropylenes and polyallomer containing AMA to ascertain differences in behavior of samples with different degrees of crosslinking (i.e., irradiated to different doses). For this purpose, extensive measure-

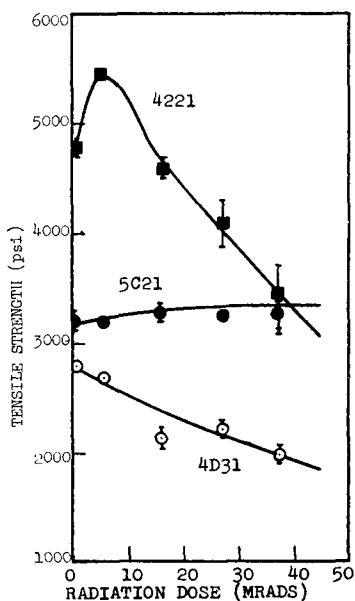


Fig. 2. Tensile strength vs. machine radiation dose for polypropylenes. Straight irradiation.

ments were performed at 180°C, a temperature at which no crystallinity remains.

Curves of creep compliance versus time for polypropylenes 4D31, 4221, and polyallomer 5C21 were obtained at that temperature. Characteristic

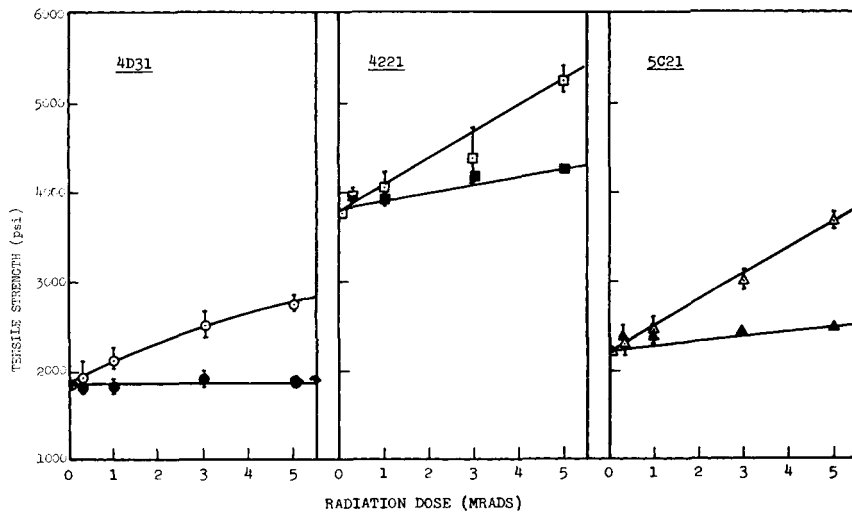


Fig. 3. Tensile strength vs. ⁶⁰Co radiation dose for polypropylenes: (O, □, Δ) with AMA; (●, ■, ▲) without AMA.

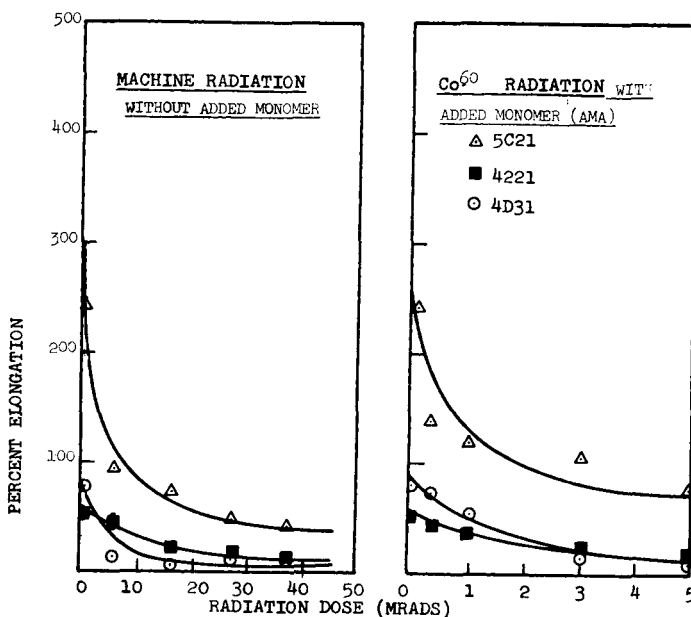


Fig. 4. Radiation dose vs. per cent elongation for polypropylenes: (a) machine radiations without added monomer; (b) ⁶⁰Co radiation with added monomer (AMA).

curves were obtained from composite raw data for four to six test specimens as shown in Figure 5 for Tenite 4221/AMA. Although an increase in compliance with time is noted, the rate of increase decreases as the test duration increases. With a load of 7.9 psi imposed on specimens irradiated to

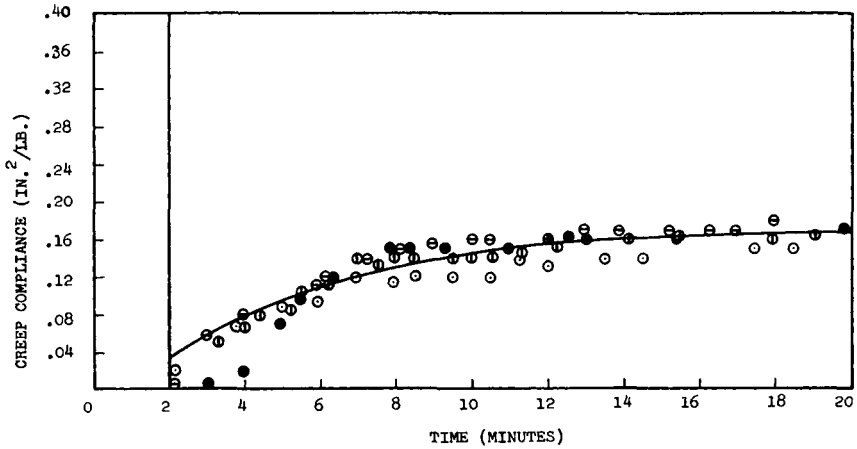


Fig. 5. Creep compliance vs. time for four polypropylene 4221/AMA samples irradiated to 1 Mrad and tested at 185°C; load = 7.9 ± 0.1 psi; plot of raw data.

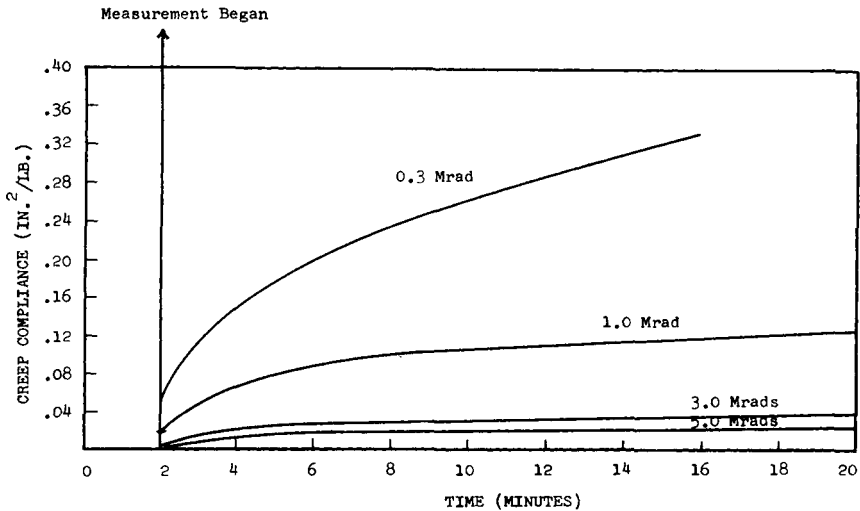


Fig. 6. Creep compliance vs. time for polypropylene 4D31/AMA ($7.1 \pm 0.5\%$) systems irradiated to 0.3–5.0 Mrad and tested at 185°C; load = 7.4 ± 0.4 psi.

1 Mrad the curve indicates considerable leveling off after 10–15 min. Subsequent creep curves also represent the composite data for four to six individual test samples and experimental points will be omitted to eliminate cluttering and to facilitate evaluation and comparison of data.

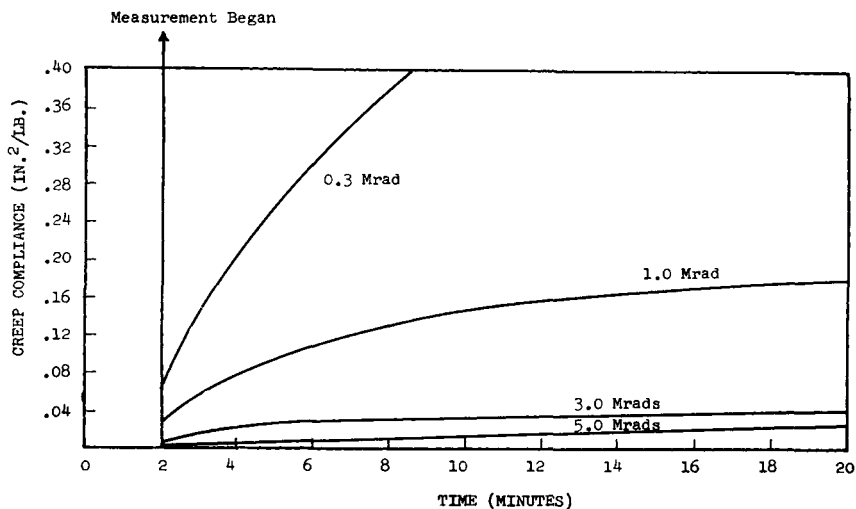


Fig. 7. Creep compliance vs. time for polypropylene 4221/AMA (4.3 ± 0.4%) systems irradiated to 0.3–5.0 Mrad and tested at 185°C; load = 7.9 ± 0.1 psi.

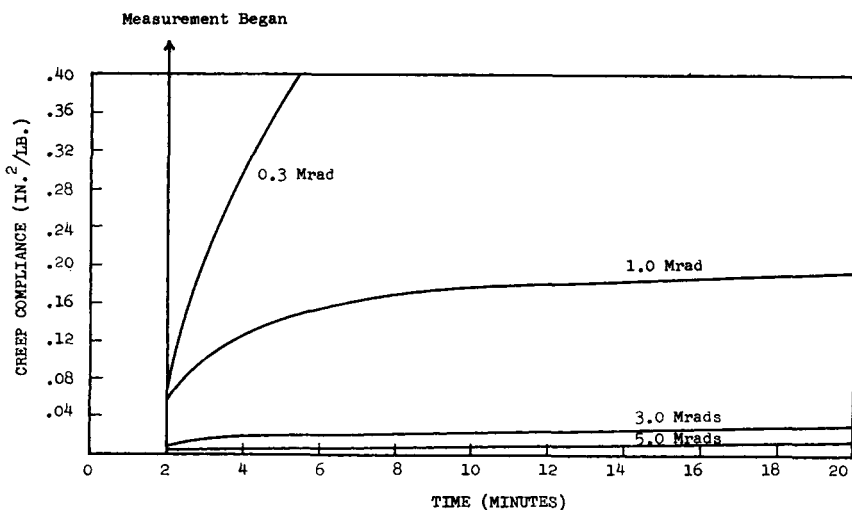


Fig. 8. Creep compliance vs. time for polypropylene 5C21/AMA (69%) systems irradiated to 0.3–5.0 Mrad and tested at 185°C; load = 8.0 ± 0.1 psi.

The polypropylene systems containing AMA and irradiated to 0.3, 1.0, 3.0, and 5.0 Mrads are shown in Figures 6, 7, and 8. These curves show that for these crosslinked hydrocarbon polymers, creep occurred most rapidly at the lowest dose and progressively decreased with increasing dose. Since these measurements were made under conditions where no crystallinity was present, the differences must necessarily have been due solely to differences in the degrees of crosslinking. It is to be noted that polypropylene samples that were unirradiated or irradiated to these same doses

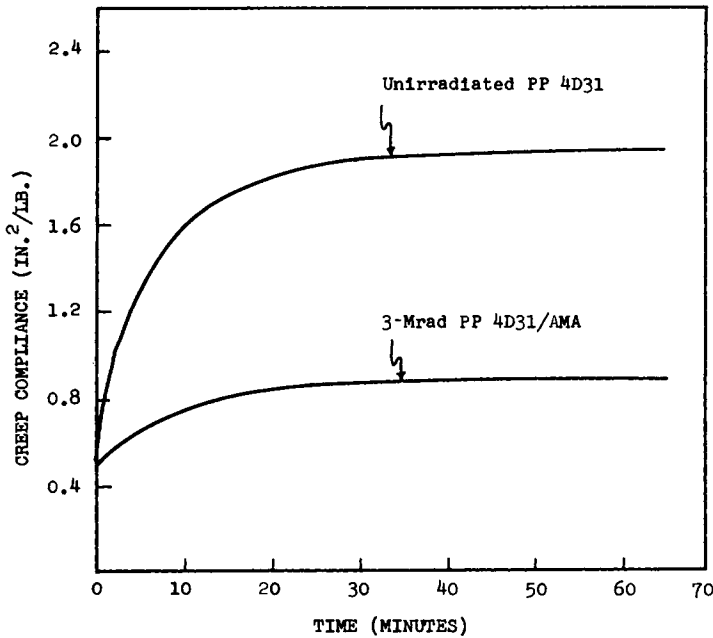


Fig. 9. Creep compliance vs. time at 145°C for unirradiated polypropylene 4D31 and for 4D31/AMA irradiated to 3 Mrad; load = 10.4 psi.

in the absence of allyl methacrylate, could not withstand the static loads and stretched to failure in less than two minutes under identical conditions of testing.

Table I compares creep compliance of AMA-containing systems after 5 min at 185°C. These data clearly indicate that the degree of crosslinking of the polymers can be readily distinguished by creep measurements of samples in the rubbery state.

TABLE I

Five-Minute Creep Compliance of Polypropylene/AMA at 185°C, load = 7.4-8.0 psi

Polymer	Dose, Mrad	Compliance, in. ² /lb
4D31	0.3	0.17
	1.0	0.08
	3.0	0.03
	5.0	0.02
	5.0	0.01
4221	0.3	0.26
	1.0	0.10
	3.0	0.03
	5.0	0.01
5C21	0.3	0.37
	1.0	0.14
	3.0	0.02
	5.0	0.01

Similar measurements performed on polypropylene 4D31 at 145°C are shown in Figure 9. At this temperature, unirradiated polypropylene retains some crystallinity and hence survived the creep test; compliance of the uncrosslinked, partially crystalline system could therefore be quantitatively compared with the crosslinked (3 Mrad in the presence of AMA), partially crystalline system. It can be seen that despite the residual crystallinity, the monomer-containing, irradiated system exhibited significantly less compliance than the unirradiated samples. Under these test

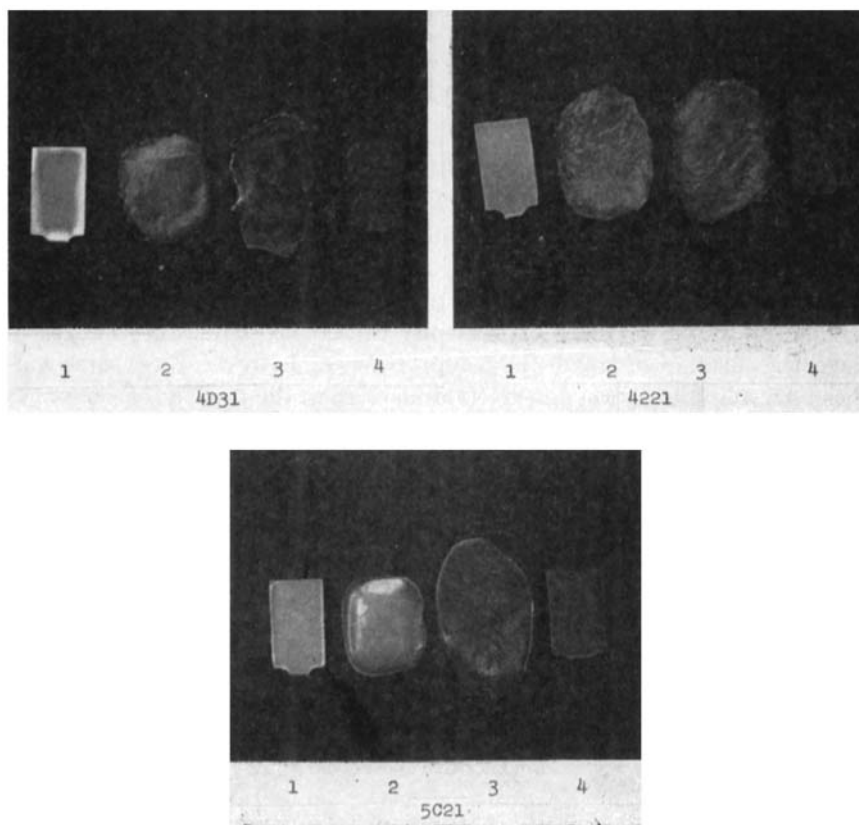


Fig. 10. Heat stability of crosslinked polypropylenes: (1) unheated, unirradiated control; (2) heated (214°C, 1 hr), unirradiated control; (3) heated (214°C, 1 hr), irradiated (5.0 Mrad), no AMA; (4) heated (214°C, 1 hr), irradiated (5.0 Mrad), with AMA.

conditions, the compliance of the untreated polymer increased from 0.5 to 1.9 in.²/lb within 1 hr while that of the crosslinked system increased to only 0.9 in.²/lb. At 145°C monomer-free systems irradiated to 3 Mrad stretched and broke in less than 2¹/₂ min, probably because of the reduction in crystallinity and polymer chain length, both resulting from the irradiation; therefore, no attempt was made to measure their creep compliance quantitatively.

Heat Stability of Crosslinked Polypropylenes

Figure 10 shows the results of heat treatment (one hour at 214°C) on the crosslinked polypropylenes. All three AMA-containing polymers irradiated to 5 Mrads retained their form stability. Specimens that were not irradiated or those irradiated to 5 Mrad in the absence of AMA did not maintain their form stability and flowed under the heating conditions. The 5-Mrad, monomer-free samples exhibited more pronounced flow and poorer form stability than the unirradiated specimens; this again demonstrates the degradative effect of radiation of polypropylenes in the absence of monomer.

Dielectric Properties

Tables II, III, and IV list the dielectric properties of the irradiated and unirradiated polypropylenes. It will be noted, that all unirradiated specimens had low dielectric constants ($K = 2.2$ - 2.3) and dissipation factors ($\tan \delta = 0.0006$ or less). No significant change in either the dielectric constant or the dissipation factor resulted from irradiation of monomer-free specimens, whether carried out in air or in nitrogen. Similarly, ^{60}Co irradiation in the presence of monomer caused no significant changes in dielectric constant of any of the polypropylenes; however, these same conditions resulted in a two- to threefold increase in the dissipation factors of 4D31 (polyisobutylene-modified polypropylene) and 5C21 (polyallomer) grades but not of the 4221 (straight polypropylene) grades. These increases in $\tan \delta$ became apparent at dose levels of 1-3 Mrads. It should be noted that the quantity of monomer incorporated in the irradiated grades

TABLE II
Dielectric Properties of Irradiated Polypropylene 4D31

Radiation		Dielectric constant K			Dissipation factor $\tan \delta$		
Dose, Mrad	Source	1 kHz	100 kHz	1 MHz	1 kHz	100 kHz	1 MHz
Monomer-free specimens							
0	—	2.26	2.26	2.27	0.0001	0.0002	0.0004
16	Machine	2.30	2.29	2.30	0.0004	0.0004	0.0007
26.7	"	2.31	2.31	2.31	0.0003	0.0003	0.0004
37.3	"	2.29	2.29	2.29	0.0005	0.0005	0.0005
0.3	^{60}Co	2.29	2.28	2.26	0.0005	0.0005	0.0005
1.0	"	2.29	2.29	2.29	0.0005	0.0005	0.0005
3.0	"	2.30	2.29	2.29	0.0005	0.0005	0.0005
5.0	"	2.29	2.29	2.28	0.0005	0.0005	0.0005
Monomer-containing specimens (6.5 ± 1% AMA)							
0.3	^{60}Co	2.32	2.31	2.31	0.0004	0.0004	0.0005
1.0	"	2.32	2.31	2.31	0.0014	0.0009	0.0011
3.0	"	2.32	2.31	2.32	0.0014	0.0009	0.0005
5.0	"	2.32	2.32	2.31	0.0014	0.0009	0.0005

4D31 and 5C21 was greater than that in irradiated grade 4221 polypropylene. Therefore, the change in dielectric losses here appears to be related to the incorporated monomer level. To impart improved physical proper-

TABLE III
Dielectrical Properties of Irradiated Polypropylene 4221

Radiation		Dielectric constant K			Dissipation factor $\tan \delta$		
Dose, Mrad	Source	1 kHz	100 kHz	1 MHz	1 kHz	100 kHz	1 MHz
Monomer-free specimens							
0	—	2.31	2.30	2.30	0.0003	0.0003	0.0003
5.3	Machine	2.29	2.29	2.29	0.0002	0.0003	0.0003
16	"	2.29	2.29	2.28	0.0002	0.0003	0.0003
26.7	"	2.30	2.29	2.29	0.0003	0.0003	0.0003
37.3	"	2.27	2.27	2.27	0.0003	0.0002	0.0003
0.3	^{60}Co	2.28	2.28	2.26	0.0004	0.0004	0.0005
1.0	"	2.28	2.28	2.29	0.0004	0.0004	0.0005
3.0	"	2.28	2.28	2.29	0.0004	0.0004	0.0005
5.0	"	2.28	2.28	2.27	0.0004	0.0005	0.0005
Monomer-containing specimens ($3.4 \pm 0.7\%$ AMA)							
0.3	^{60}Co	2.30	2.29	2.31	0.0004	0.0004	0.0005
1.0	"	2.32	2.31	2.31	0.0004	0.0004	0.0005
3.0	"	2.30	2.29	2.28	0.0009	0.0005	0.0005
5.0	"	2.30	2.29	2.29	0.0004	0.0004	0.0005

TABLE IV
Dielectrical Properties of Irradiated Polyallomer 5C21

Radiation		Dielectric constant K			Dissipation factor $\tan \delta$		
Dose, Mrad	Source	1 kHz	100 kHz	1 MHz	1 kHz	100 kHz	1 MHz
Monomer-free specimens							
0	—	2.25	2.26	2.24	0.0002	0.0006	0.0004
5.3	Machine	2.29	2.29	2.28	0.0003	0.0004	0.0004
16	"	2.30	2.29	2.28	0.0005	0.0005	0.0004
26.7	"	2.30	2.30	2.29	0.0005	0.0005	0.0006
37	"	2.30	2.29	2.29	0.0005	0.0005	0.0006
0.3	^{60}Co	2.26	2.26	2.26	0.0005	0.0005	0.0005
1.0	"	2.27	2.26	2.26	0.0005	0.0005	0.0005
3.0	"	2.27	2.27	2.28	0.0005	0.0005	0.0005
5.0	"	2.27	2.26	2.27	0.0005	0.0005	0.0005
Monomer-containing specimens ($6.5 \pm 0.7\%$ AMA)							
0.3	^{60}Co	2.28	2.28	2.28	0.0005	0.0005	0.0005
1.0	"	2.29	2.28	2.28	0.0005	0.0005	0.0005
3.0	"	2.30	2.29	2.30	0.0018	0.0014	0.0011
5.0	"	2.32	2.29	2.29	0.0018	0.0018	0.0011

ties without increasing dielectric losses, a maximum monomer level of 3-4% appears to be desirable.

No specific information was available as to antioxidant composition or concentration in any of the polypropylenes employed in this work. However, it is a virtual certainty that these proprietary materials do have incorporated in them small quantities of typical, commercial antioxidants. Wright¹¹ imputes power factor changes in electron-irradiated polyethylene to the decomposition of antioxidants. It is noteworthy that in the present work dielectric loss change due to irradiation of polypropylenes is negligible. From this, one tends to conclude (a) that at the radiation levels used in our work little if any antioxidant decomposed into polar products, and (b) that antioxidant continued to be effective in withstanding post-irradiation oxidation.

CONCLUSIONS

Polypropylene (Tenite 4D31 and 4221) and a polyallomer (Tenite 5C21), all stereoregular hydrocarbon polymers, can be crosslinked, and thereby thermally upgraded, by ⁶⁰Co-irradiation in nitrogen when allyl methacrylate is incorporated prior to irradiation. The creep compliance of the crosslinked systems can be determined as a function of testing time under load; at a constant testing load and monomer level, compliance at 185°C decreases with increasing dose. Since, at that temperature, the polymers behave as crosslinked elastomers, the differences in curves of compliance versus time represent differences in crosslink densities.⁶⁰ Co doses of 0.3-5.0 Mrad have been employed; the order of rate of decrease of compliance as a function of increasing dose is Tenite 4D31 > 4221 > 5C21, (under a load of 7.4-8.0 psi) indicated that the first hydrocarbon polymer crosslinks most efficiently and the last polymer least efficiently under these conditions. Both the irradiated polymer and monomer-free irradiated polymer merely melt and flow when subjected to 1 hr at 214°C while irradiated polymer with monomer retains its form, contributing further to evidence of crosslinking of the monomer-containing systems. At a lower test temperature (e.g., 145°C) at which some polypropylene crystallinity remains, the resistance of unirradiated systems to creep is due to this crystallinity whereas that of irradiated, monomer-bearing systems is due to crosslinking in addition to crystallinity as is indicated by a higher resistance to creep.

Tensile strength and gel fractions of monomer-crosslinked systems increase with dose up to 5 Mrad. Irradiation to 5 Mrad causes the tensile strength of the 4D31 and 4221 grades to increase by 30-35%, and of the 5C21 grade to increase by more than 45%. Incipient gelation occurs after less than 0.3 Mrad; after 5 Mrads, 80% gel is obtained. In the absence of AMA, irradiation does not impart similar changes to these hydrocarbon polymers; indeed, both ⁶⁰Co irradiation in nitrogen (to 5 Mrad) and machine irradiation in air (to 37 Mrad) cause decreases in tensile strength and no gelation.

Within the range of irradiation levels employed, the dielectric constants of all the polypropylene grades were unaffected whether irradiation was carried out in air or nitrogen and whether or not monomer was present. The dissipation factors of Tenite grades 4D31 and 5C21 (containing $6.5 \pm 1\%$ AMA) but not grade 4221 (containing only $3.4 \pm 0.7\%$ AMA) increased two to three-fold when irradiated to dose levels of 1 to 3 Mrads. Hence, critical dielectric applications (e.g., microwave striplines) would appear to demand that the AMA level after swelling the irradiation be held to a maximum of 4% .

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All trade names are given for identification purposes only and does not constitute an official endorsement of the material or equipment.

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