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Determining the method of crosslinking used in polyolefins

Gordon Thomas McCarty
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Determining the method of crosslinking used in polyolefins

McCarty, Gordon Thomas, M.S.

San Jose State University, 1992

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DETERMINING THE METHOD OF CROSSLINKING
USED IN POLYOLEFINS

A Thesis
Presented to
The Faculty of the Department of Chemistry
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Gordon Thomas McCarty
August, 1992

Approved for the Department of Chemistry

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ABSTRACT

Methods of crosslinking have been developed over the past 30 years for the purpose of improving the physical properties of polyolefins. With the wide and growing applications of crosslinking in the polymer industry, the need has arisen for identifying the type of crosslinking used. A technique such as this can not only assist us in staying abreast of the existing manufacturing technologies while maintaining an awareness of any new changes; but also, it can aid us first in monitoring the sterilization processes for materials used in the medical industry and second in predicting product performance of self regulating heaters based on carbon filled polymer systems. Although much attention has been given to studying physical and chemical changes resulting from crosslinking, little has been given to distinctions between the methods of crosslinking.

In this study four commonly used methods of crosslinking were applied to polyethylene and polyethylene/copolymer blends to investigate and compare the crosslinking effects each method had on polymer gel (crosslinking efficiency), unsaturation, oxidation, melting point and crystallinity. The four crosslinking methods applied to the polymers were irradiation by electron beam, ^{60}Co in nitrogen atmosphere, ^{60}Co in air atmosphere and chemical curing with peroxides.

In this study, it was shown that a combination of tests permits limited success in differentiating between the methods of crosslinking used in the polyethylene and polyethylene blends examined. All chemically crosslinked test samples provided higher gel data and lower spectroscopic ratio values for both the ketone carbonyl and trans-vinylene absorption bands. Two dimensional plotting of these characteristics displayed an isolated cluster of data points for chemically crosslinked samples. Polymers irradiated by ^{60}Co in

air also tended to cluster into an isolated group due to lower percent gel data and high spectroscopic ratio values for the ketone carbonyl absorption band. In addition, they tended to display two phase crystallization when cooled from the melt. But, all distinctions became less obvious to non existent below 20 Mrads dose. Finally, with the data collected in this study, no significant distinction could be made between samples irradiated by electron beam and those irradiated by ^{60}Co in nitrogen.

INTRODUCTION

Homopolymers and copolymers of ethylene may be crosslinked by irradiation or chemical reaction. Both techniques create free radicals which form inter- and intramolecular bonds to create a network polymer. Thus, crosslinked polyethylene, ethylene copolymers, or blends of ethylene based copolymers with polyethylene acquire a unique property of behavior. The polymer or polymer blends are semicrystalline below the melting point and elastomeric above the melting point (1). These properties make possible the characteristic called elastic memory. In addition, crosslinking has been used to improve thermal stability, chemical resistance, dimensional stability, stress crack resistance, creep resistance, tensile strength, impact resistance, and printability of plastics. As a result of these improved physical and mechanical properties, polymer crosslinking plays an important role in the packaging, tubing, piping, electrical, wire and cable industries (2,3). Some specific examples of products available only because of the properties resulting from crosslinking include: electrical end seals, molded parts, solder sleeves, heat shrinkable tubes for splicing, heat and/or solvent expandable tubes for medical applications, and electrically stable, semiconductive, carbon black filled polymers for heater systems or heat sensor switches.

Because polymer crosslinking has provided a diversity of finished products with a variety of improvements in physical and mechanical properties, the need has arisen for a method of determining the type of crosslinking used in manufacturing these polymer products. Examples of potential applications of a test such as this are discussed below.

Any polymer product for a medical application inside the human body cannot contain additives which could be leached out of the polymer into the body system. Because of the elastic memory and the swelling properties in crosslinked polymers, a recent medical application has been intravenous polymer tubes. These can be surgically inserted into a blocked artery. Upon absorption of body heat and/or moisture, the polymer tube will expand and open the blocked artery. If a polymer has been chemically crosslinked, it will contain peroxide by-products and probably residual peroxide. In addition,

medical sterilization of polymeric materials (4) requires the use of either ethylene oxide or gamma radiation. A method for determining the type of crosslinking could be used by the medical industry not only to prevent polymers containing peroxide residues from entering the body, but also to trace the sterilization technique.

Second, radiation crosslinking is used to improve the mechanical, thermal and electrical stability of self regulating heaters based on carbon black filled polymers. Crosslinking with radiation provides more desirable properties with better predictability and uniformity in performance than do chemical crosslinking methods. Successful application of radiation crosslinking to conductive polymer based heaters requires careful control, evaluation and characterization of the manufacturing and irradiation process variables to obtain optimum performance. Heater evaluation by thermal aging with a rated voltage applied often requires as much as 2000 hours testing before sufficient data has been collected for an Arrhenius plot to predict the product performance. A test method for determining the type of crosslinking could quickly screen out chemically crosslinked conductive polymer systems which are known to have poorer performance (5).

Finally, there is a general need for understanding manufacturing procedures after the fact. This is important in monitoring competition by not only seeking sales advantages and patent protection, but also by conducting what has been referred to as reverse engineering. With this comes a broadened knowledge of technical advances and the potential for improvement of existing products.

Irradiation with high energy electron beams, gamma-radiation with ^{60}Co , and chemical curing of peroxides are the three methods of polymer crosslinking most used in industry today. Although all three methods produce materials of similar physical properties, each have unique differences providing advantages and disadvantages. Electron beams accelerate a dense population of electrons which can deliver a radiation dose of about one Megarad (Mrad) every five seconds. But, since the sample is being bombarded with particles, the penetration is relatively low (about 5 mm). ^{60}Co delivers gamma rays at a dose

rate of only 1 to 2 Mrads per hour, but has penetration up to several centimeters. Chemical curing requires premixing a peroxide with the polymer, heating it above the melt in a mold, and curing it at temperature for a specified time. This provides uniform crosslinking without concern for depth of penetration.

A Mrad is 10^6 rads, where a rad is defined as being the absorption of 100 ergs energy per gram of material. Since this is a cumulative property, a Mrad exposure at high rate from an electron beam would be equivalent to a Mrad exposure at a low rate from ^{60}Co (6).

In order to design an experiment for differentiating between these crosslinking methods, we must first be aware of what reactions occur during the process and second, compare the expected differences. It is well known from work conducted over the past thirty years that at least three additional reactions occur during the crosslinking process. They are: formation of main chain unsaturation, decomposition by either chain scission or oxidation and, in the case of chemical crosslinking, homolytic cleavage of the peroxides.

Bombardment with high energy electrons or gamma-rays causes both ionization and excitation. Two radical processes are believed to take place. The first occurs as a result of a free radical remaining on the main chain where a "hot" hydrogen has been released. This "hot" hydrogen atom will react immediately with another nearby hydrogen attached to either an adjacent chain molecule to form a crosslink, or to the adjacent carbon on the same chain to form a point of unsaturation (6).

The second requires migration of the radical sites, produced by C-H bond cleavage, along the polymer chains until two are adjacent. Again, if the adjacent radicals are on neighboring chains, a crosslink forms. If they are on the same molecular chain, unsaturation forms (7). This theory of migrating radical sites has been supported by results from spectroscopic examination of an absorption band (73 cm^{-1}) associated with lattice chain vibrations within the crystalline region of polyethylene. Since radiation had little effect on this band, it was hypothesized that crosslinking occurred only in the amorphous regions, while the crystalline regions were mostly unaffected (8). Therefore, radicals created in the crystalline region would migrate along the chain to the amorphous region before reacting. During this migration process, there would be increased probability of two radicals on the same chain coming together to form an unsaturated bond.

In contrast, the reaction mechanism of chemically crosslinked polymers produces an almost immeasurable quantity of unsaturation. When heat cured, the polymer is above its melting point in a totally amorphous state. At this temperature, the peroxides used to initiate chemical crosslinking undergo homolytic cleavage forming free radicals which would be more stable if combined with a hydrogen atom. Therefore, they randomly strip hydrogen atoms from the polymer chain (9). Because of this random removal of hydrogen, there is a uniform distribution of crosslinks throughout the polymer. There is, also, a low probability of stripping hydrogen atoms from two adjacent carbons allowing the formation of an unsaturated bond.

Both crosslinking and degradation have been observed to occur simultaneously in polyethylene when the polymer is irradiated in the presence of oxygen (10). Dose rate has been found to play an important role in the amount of oxidation which occurs. This is due to the rate of oxygen diffusion into the polymer. If irradiation is conducted at high dose rates, the oxygen initially present in the polymer is rapidly consumed. Irradiation thereafter takes place as if in the absence of oxygen. However, at low dose rates, oxygen is consumed slowly, allowing diffusion to provide a constant supply of oxygen during irradiation (6).

Oxidative degradation of irradiated polymers generally proceeds through free radical reactions forming a peroxide or hydroperoxide at the site where hydrogen detachment occurred. Secondary decomposition yields a variety of products containing carbonyl, carboxyl and hydroxyl groups. Some typical examples of reactions are (11,12):

Peroxide curing agents are selected on the basis of their most desirable decomposition temperature. The most widely used are dicumyl peroxide, benzoyl peroxide, and di-t-butyl peroxide. Their structures and expected by-products are (13):

A substantial amount of work has gone into studying the effects of variables such as dose, dose rate, oxygen, temperature and peroxide levels on the physical and mechanical properties for the individual crosslinking techniques. In contrast, efforts comparing the techniques and their effects has been relatively sparse. There is no single source which sufficiently compares these three crosslinking techniques and their effects such that it enables the correlation of distinguishing characteristics for determining the type of crosslinking used. Therefore, the following tables have been compiled from a variety of sources in order to make these comparisons.

TABLE I: Detection methods and observed differences in chemical vs. radiation crosslinked polyolefins.

CHEMICAL EVENT	CROSSLINKING METHOD		OBSERVED DIFFERENCES	DETECTION METHOD
	RADIATION	CHEMICAL		
CROSSLINKING	YES	YES	MORPHOLOGY CRYSTALLINITY	DSC, XRD SEM (14,15)
UNSATURATION	YES	TRACE	TRANS-VINYLENE	IR, NMR (16,6)
DECOMPOSITION CHAIN SCISSION	YES	TRACE (15)	CH ₂ , CH ₃ RATIO (10, 6)	IR, NMR (17)
OXIDATION	YES	NO	CARBONYL, CARBOXYL, HYDROXIDE GROUPS (6)	IR, NMR (10)
PEROXIDE BY- PRODUCTS	NONE	YES	DEPENDS ON PEROXIDE USED	IR, NMR (15)

Table I compares the chemical events which occur during radiation crosslinking versus chemical crosslinking. It also lists the differences and their possible methods of detection. Although there are several, the two most striking differences are the trans-vinylene unsaturation and the peroxide by-products. Measurement of trans-vinylene by infrared spectroscopy should be useful because it is a tried and proven method for quantitating radiation dose. Detection of peroxide by-products would be useful because of its ability to show direct evidence of a peroxide. This, however, would probably require additional separation steps due to expected low concentrations. Measurement of oxidation by infrared spectroscopy could also provide beneficial information; especially in the pure polyethylenes. This may not be possible with copolymers or copolymer blends due to masking of the oxidation by the existing carbonyl bands.

In like manner, Table II lists the observed differences one would expect and the detection method for electron beamed polymers vs. ^{60}Co gamma - irradiated polymers. From it we see that the same chemical events occur from the two irradiation techniques (10). The only major difference relates to the amount of oxidation which occurs during radiation. Oxidation is a surface phenomenon dependant upon the dose rate and the atmosphere in which irradiation is conducted (6).

Trans-vinylene, peroxide by-products and degree of oxidation stand out as potentially the most detectable chemical events. All three can be measured by infrared spectroscopy. Table III lists absorption bands where intensity changes have been observed by infrared spectra of irradiated polyethylene films (18).

TABLE II: Detection methods of expected differences in irradiated polymers

CHEMICAL EVENT	CROSSLINKING METHOD		OBSERVED DIFFERENCES	DETECTION METHOD
	ELECTRON BEAM	COBALT		
CROSSLINKING	HIGH DOSE RATE	LOW DOSE RATE	OXIDATION	IR NMR
UNSATURATION	YES	YES	NONE	N/A
DECOMPOSITION CHAIN SCISSION	YES	YES	NONE	N/A
OXIDATION	YES	YES	DEPENDS ON DOSE RATE AND ATMOSPHERE (19)	IR, ATR IR NMR ESCA (20)

Of these numerous absorption bands, the trans-vinylene and ketone carbonyl are the most likely to provide useful information. The absorption bands of the copolymers will mask the frequencies from 1000 to 1500 cm^{-1} and 1720 to 1750 cm^{-1} .

The trans-vinylene absorption band at 965 cm^{-1} could be extremely helpful in providing information not only because of the previously mentioned differences in reaction mechanisms, but also because of the relatively strong intensity of this band. Apart from crosslinking, the formation of main chain unsaturation is one of the most noticeable chemical changes which occurs in an irradiated polymer (10). Of the absorption bands providing information about chemical change, the trans-vinylene band is probably the strongest and easiest to observe. As a result, spectroscopic measurement of this peak has been used for quantitating irradiation dose (16).

TABLE III: Observed changes in infrared spectra of irradiated polyethylene films

Frequency (cm ⁻¹)	Assignment	Description
1742	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{H} \end{array}$	aldehyde carbonyl
1716	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{R}' \end{array}$	ketone carbonyl
1642, 991, 909	$\text{R}-\text{CH}=\text{CH}_2$	terminal vinyl
1378	$\text{R}-\text{CH}_3$	secondary bending
1368, 1353, 1308, 1261 & 800	$-\text{CH}_2-$	amorphous phase
1131, 1068	$\text{C}-\text{O}-\text{C}$	ketals
965	$\text{R}-\text{CH}=\text{CH}-\text{R}'$	trans-vinylene
890	$2\text{R}-\text{CH}=\text{CH}_2$	terminal methyl (21)
675-730	$\text{R}-\text{CH}=\text{CH}-\text{R}'$	cis-vinylene (21)

Both crosslinking and degradation occur simultaneously in polyethylene when it is irradiated in the presence of oxygen. Irradiation in air causes a drastic change in the absorption bands associated with the ketonic carbonyl groups (1716 cm⁻¹). These chemical changes are indicative of oxidative degradation (20).

As stated previously, the atmosphere and dose rate due to oxygen diffusion play important roles in the amount of oxidation which occurs. Since ⁶⁰Co irradiation takes place at a low dose rate, one way to minimize the oxidation effect is to conduct irradiation in the absence of oxygen. There are some applications such as sterilization of syringes or other small medical items

where prepackaging and irradiation in the absence of oxygen would be feasible. However, there are other situations such as continuous production or long tube production where it would not be feasible. The ketone carbonyl band should be useful in distinguishing between the three types of irradiation: ^{60}Co , low dose rate in air; electron beam, high dose rate in air; and ^{60}Co , low dose rate in the absence of oxygen.

In this study, eight different polymer formulations were made with and without peroxide curing agents such as dicumyl peroxide or benzoyl peroxide. These eight formulations consisted of high density polyethylene (HDPE), low density polyethylene (LDPE), poly (ethylene-co-ethylacrylate) (EEA), poly (ethylene-co-vinylacetate) (EVA), 50:50 of HDPE plus EVA, HDPE plus EEA, LDPE plus EVA and LDPE plus EEA. All formulations were then crosslinked by each of the three methods previously mentioned. The irradiated samples were given 0, 5, 10, 20, 40 and 80 Megarad doses. Several methods of infrared spectroscopy were conducted to characterize the type of crosslinking applied to each sample.

All initial development work for the irradiated samples was done on those having received an 80 Mrad dose with zero as the control. Once a method was established, the procedure was applied to the 5 Mrad sample. If successful, no further work would be necessary for the 10, 20, and 40 Mrad samples. If not successful, the intermediate dose samples would have to be tested to determine the limits of the technique.

From the previously tabulated comparisons, unsaturation in the irradiated samples, oxidation in the gamma-irradiated samples and peroxide by-products in the chemically crosslinked samples are characteristics expected to be unique to each crosslinking procedure. These characteristics became the basis of the analytical scheme. However, since this test will ultimately be applied to complex formulations containing numerous potentially interfering additives, verification of radiation induced unsaturation in the solvent soluble fraction of the polymer (10) is necessary. To do so, a spectral comparison of the trans-vinylene absorption band must be made between the uncrosslinked, the crosslinked, and the solvent extract of the crosslinked polymers.

Infrared spectra were taken from a solvent cast film of the soluble extracts. These spectra were examined for the presence of unsaturation and ketone carbonyl bands in an effort to separate the radiation crosslinked from the chemically crosslinked polymers. Characterization by solid state ^{13}C NMR was also attempted.

The purpose of this research project is to sort from the literature unique and potentially measurable differences in these different types of crosslinking. A method could then be developed to characterize the crosslinking technique used in raw polyethylene and copolymer blends with polyethylene. The method could then be extended and applied to the complex formulations one might find in industry.

EXPERIMENTAL

2.1 Materials

The six materials used are all commercially available. Their selection was based solely upon being readily available to the author. Those selected are listed below with their vendors. Also listed are the abbreviated names to which these products will be referred throughout the remainder of this paper.

Table IV: Materials and Vendors

Materials Tested	Abbreviated Name	Manufacturer
Alathon 7050	HDPE #1	DuPont
Petrothene NA-271	LDPE #1	USI
DPD 6169	EEA	Union Carbide
Elvax 450	EVA	DuPont
Marlex 6003	HDPE #2	Phillips Chem. Co.
DFD 6040	LDPE #2	Union Carbide

The latter two high and low-density polyethylenes were introduced later in the experimentation to determine the consistency of some of the observed differences.

2.2 Blend Preparation

Approximately 200 gram batches of samples were weighed for mixing by a twin screw Brabender (Model OCC) in a 250 cc mixing bowl. The quantity of

each batch was determined by calculating the weight of sample, based on specific gravity, necessary to fill the mixing bowl to 90 percent capacity. The blends consisted of a 1:1 weight ratio. The following batches were made.

Table V: Sample Blends Prepared

Component A	Component B	Batch Wt. (gms)
HDPE #1		216.0
LDPE #1		209.0
HDPE #1	EVA	214.0 (107 gms. each)
HDPE #1	EEA	213.0 (106.5 gms. each)
LDPE #1	EVA	210.4 (105.2 gms. each)
LDPE #1	EEA	209.2 (104.6 gms. each)
EVA		211.0
EEA		209.0
HDPE #2		216.0
LDPE #2		209.0

For consistency of processing history, all pure and blended samples were mixed in the Brabender with similar conditions. Sample pellets were gradually added to the 175°C preheated mixing chamber with a 15 rpm. screw speed, until the pellets blocked the top of the mixing bowl. After about 15 seconds, the pellets were drawn into the chamber. At this point, more material was added. This process was continued until the entire preweighed sample was in the mixing bowl. The RPM was increased to 40 giving a torque reading of about 4000 to 4500 ft. lbs. During the next three to five minutes of mixing, the torque decreased and reached a low plateau of about 2500 ft. lbs. as the sample batch became totally molten and blended. After reaching constant

torque at 40 rpm, mixing was continued for 5 minutes. The total Brabender mixing time was about 15 minutes per batch.

In preparation for the next batch, the blended samples were removed as rapidly as possible and allowed to cool to room temperature. Spectral examination of the batches revealed that flushing with a sample of the next blend was insufficient to prevent cross contamination. Therefore, extra caution was necessary. The mixing bowl was dismantled, cleaned with a wire bristle brush, reassembled and flushed prior to addition of the next batch.

A second set of blends composed of the same polymers with the same blend ratios were mixed with 2% by weight Dicumyl Peroxide on a 3 inch, two roll steam mill. The total mixing time was again 15 minutes. This method of mixing the peroxide blends was chosen because of their sensitivity to time at a given temperature. The temperature of the mill was more easily controlled and, once blended, the materials could be more rapidly removed from the heat zones. Again, thorough cleaning was necessary after each batch.

The preweighed, lower melting constituent was added to the mill preheated to 140°C, allowed to melt, then the higher melting constituent was added. After melting, the temperature was lowered to 120°C. At this temperature, the polymers were not as sticky and were more workable. Mixing was done by scraping the molten blend from one side of the roller and folding it over to the other in a crisscross motion.

After thoroughly mixing the polymers, the dicumyl peroxide was added at temperatures between 115 and 120°C as specified by Hercules Technical literature (22). Mixing was continued for two minutes, after which the steam was turned off. After an additional two minutes, the temperature had dropped to 98 to 105°C. At this temperature, the polymers began to solidify and peel from the rollers for easy, rapid removal.

Twelve 6" x 6" slabs of each Brabender blend were compression molded between teflon lined steel plates in a Pasadina Hydraulics (PHI) eight inch platen, electric heat press at 195°C and 38,000 psi. for ten minutes. They were then quenched by immediately transferring the steel plate mold into an eight inch platen water cooled press with 38,000 psi applied until cooled to room

temperature (approximately two minutes). Thick 20 mil. films were made so that minimal spectral changes could be easily detected.

2.3 Crosslinking

2.3a Chemical Crosslinking

Two 6" x 6" slabs of each of the milled blends containing peroxide were prepared in a manner similar to the Brabender blends. Control of time and temperature were critical factors since the polymer blends were being crosslinked while simultaneously being pressed into slabs. According to product literature (9), the estimated half life for dicumyl peroxide is 0.6 minutes at 195°C. Therefore, a minimum cure time of 5 minutes is recommended for 99.2% consumption of the peroxide. For consistency in this work, the time was extended to ten minutes at 195°C.

2.3b Electron Beam Irradiation

To assure uniform dose across the full width of the slab during irradiation, each slab was cut in half forming two 3" x 6" slabs. They were then taped together as a pair, end-to-end, with a 2" x 2" "C stock" dosimeter between them. This dosimeter would eventually become the means of determining the actual dose received by each slab.

One pair of slabs of each blend was then taped around the circumference of a 30" diameter, 8" wide wheel placed 12" from the window of Raychem's electron beam #1. The beam is composed of a 1 Mev (800 Kev) resonant core transformer (General Electric Co.). When operated at a current of 5.0 mAmps with a wheel speed of 80 rpm., the sample receives one Mrad every 5.73 seconds. Five sets of slabs, representing all blends, were mounted around the wheel as well as an extra dosimeter. Each set of blends was then exposed to irradiation for 28.6, 57.3, 114.5, 229.2 and 458.4 seconds which represent a 5, 10, 20, 40 and 80 Mrad dose respectively. The spare dosimeter

was used as an on-line monitoring device to assure the desired beam dose was being received.

2.3c ^{60}Co Beam - Gamma Ray Irradiation

For ^{60}Co irradiation, all slabs were prepared in a manner similar to that used for the electron beam. A full set of slabs representing all blends for each dose level was placed inside a four liter beaker which was constantly flushed with nitrogen during irradiation. Extra dosimeters were also included for on-line dose monitoring. This set represented Gamma ray irradiated polymers in the absence of oxygen.

In addition, slabs of all blends were taped to the outside of the beaker for a 10 and 80 Mrad dose. Only these two dose levels were used for gamma radiation in air because of sample thickness, time and cost restrictions. If all dose levels were to be applied, the number of slabs would have created too great a thickness for uniform irradiation. Because of the amount of time and cost for this part of the experiment, the samples beamed in air were limited only to the 10 and 80 Mrad dose levels, except for HDPE #2 and LDPE #2 which were used for comparison.

The ^{60}Co source is manufactured by Atomic Energy of Canada, LTD., Model # Gamma Beam 650, Serial #6 with 1.1 to 1.7 Mev. It consists of 24 sources inside 12 tubes arranged in a 24 cm. diameter panoramic array around a rotisserie. The samples were mounted inside and outside a four liter beaker on the rotisserie placing them 5 - 6 cm from the vertical center line. The dose rate was 0.75 Mrad/hour.

2.4 Test Procedures

2.4a Percent Gel

Two 150 to 200 mgm. samples of crosslinked polymer were cut from slabs representing each dose level for each blend and method of crosslinking. The samples were carefully weighed on a five place Mettler H54AR balance,

inserted into a seamless, fabric, tubular gauze, placed in a 500 ml round bottom flask containing 250 ml xylene, and refluxed for three hours. The refluxed xylene was decanted from the flask, fresh xylene was added and the sample was refluxed over night. The next morning, the old xylene was again decanted from the flask and fresh xylene added for a 1 to 2 hour reflux rinse. After completing the reflux cycle, the Tubegauz® containing the samples was removed from the xylene, allowed to drain, and dried inside a 145°C vacuum oven overnight. The samples were removed from the oven, cooled to room temperature inside a desiccator, removed from inside the gauze, and weighed again. The percent gel is the final weight times 100 divided by the initial weight.

Samples of 5 Mrad and sometimes 10 Mrad dose levels had to be handled differently. Because of their low level of crosslinking, the Tubegauz® was too porous to retain the polymer gel. For these cases, the gel test had to be repeated using 400 mesh screen to encapsulate the gel.

2.4b Infrared Spectroscopy

All infrared spectroscopy measurements were done using a Perkin - Elmer 1430 grating spectrometer interfaced with a Perkin - Elmer 7700 data station. The instrument was checked weekly for calibration against a standard polystyrene film. In addition, this instrument and the dose measurement procedure were calibrated using a set of secondary and a set of tertiary dosimeters composed of 20 mil thick extruded sheets of "C stock" DFD 6040 polyethylene. This particular dosimeter has been used for over ten years because of its ability to tolerate and accurately measure wide dose ranges once calibrated. Other dosimeters such as: Red Perspex, blue cellophane and blue nylon which measure colorimetrically are extremely accurate, but only over narrow dose ranges from 0.1 to 5 Mrads. However, these dosimeters of the narrow range are the primary devices used to create the wide range calibration curve from the DFD 6040. The two sets of dosimeters necessary for this work ranged from 0 to 24 at 2 Mrad increments and 0 to 100 at about 10 Mrad increments.

Calibration of the dosimeters and determination of the standard graph were tedious processes requiring the use of Far West Technology's blue dyed nylon film dosimeters and assistance from the National Institute of Standards and Technology (NIST). Approximately 50 to 100 blue nylon dosimeters were randomly selected from Lot # 8W9-1 and sent to NIST. NIST then randomly separated the dosimeters into sets of five, marked them, and colorimetrically read all with a Perkin - Elmer UV/VIS Lambda 4A spectrophotometer at 510 and 605 nm wavelengths. The dosimeters were then exposed to desired dose levels of 0, 1, 3, and 5 Mrads from a NIST calibrated source. After equilibrating 24 hours under controlled temperature and humidity, each dosimeter was again colorimetrically measured and the absorptivity was recorded as an average of five dosimeters at each dose level. These exposed dosimeters were then returned, along with the NIST data (23).

Simultaneously with the calibrated source exposure and readings at NIST, a similar exposure and reading process was conducted on dosimeters from the same lot at Raychem. Upon receiving the dosimeters from NIST, both the Raychem and the NIST exposed dosimeters were read on a UV/VIS spectrophotometer identical to that used at NIST. From this, a calibration curve for the primary dosimeters was established. In addition, since simultaneous exposure and reading experiments were conducted at NIST and Raychem, any necessary changes in absorption readings due to time could be determined and factored into the calibration curve (23).

Since beam dose is an additive property, the secondary dosimeters were prepared by incremental dosimetry. Many 1 1/2" square pieces of sheet were cut from the DFD 6040 "C stock" sheet, placed inside the 4 liter beaker along with a blue nylon dosimeter, flushed with nitrogen and exposed to approximately 2 Mrads dose from the ^{60}Co source. The nylon dosimeter was removed and measured against the NIST established standard curve. One square of DFD 6040 was removed from the beaker and assigned the measured dose. A new nylon dosimeter was added to the beaker and the same process repeated. When the second 1 1/2" square was removed, it was assigned a dose equal to the sum of the two nylon dosimeter readings. This process was continued up through 24 Mrads dose (23).

The second set were tertiary dosimeters ranging from 0 to 100 Mrads calibrated in a similar manner as the first set. These, however, were made with approximately 10 Mrad increments which were measured against the 0 to 24 Mrad set.

To acquire spectroscopic ratio data, two spectral scans were conducted on each 1 1/2" square dosimeter from 2200 to 1900 cm^{-1} and 1020 to 920 cm^{-1} . The spectroscopic ratio measures light absorbance at two different wave numbers. For this study, it was the infrared light absorbance at 965 cm^{-1} divided by infrared light absorbance at 2020 cm^{-1} .

$$S_r = \frac{A(965)}{A(2020)}$$

By applying the Beer - Lambert law the equation becomes:

$$S_r = \frac{A(965)}{A(2020)} = \frac{-\log I/I_0 @ 965 \text{ cm}^{-1}}{-\log I/I_0 @ 2020 \text{ cm}^{-1}}$$

where I_0 is the maximum light transmittance or the baseline and I is the minimum light transmittance or the peak maxima.

The first of the two scans was conducted with the light pattern and spectral window parallel to the extrusion direction of the sheet. The second was perpendicular to the extrusion direction of the sheet. The S_r of these two scans was then averaged to compensate for any spectral differences which might exist due to molecular orientation. The peak at 965 cm^{-1} is the result of light absorption from the presence of the trans-vinylene bonds and increases proportional to dose. The peak at 2020 cm^{-1} is referred to as the thickness peak. This band is the result of infrared absorption from a combination of modes from polymeric crystalline vibration. Work by Tabb et al. has shown it to be unaffected by irradiation (19) since cross-linking occurs predominantly in the

amorphous phase (24). Therefore, by using an absorption band unaffected by cross-linking for calculating S_r , any variation in absorption caused by variation in film thickness would be normalized.

The resulting data (25) were tabulated and graphed (See Table IV and Fig. 1.). A best fit curve was mathematically derived from the data of the secondary dosimeters to provide the following quadratic equation.

$$\text{Dose (Mrad)} = 6.13S_r^2 + 24.15S_r - 0.83 \quad (1)$$

The fit of the data to the quadratic equation was fairly good, with a correlation coefficient of 0.9985.

Table VI: Spectroscopic Ratio of Dose Standards

Dosimeter ID	Calibrated Dose	Spectroscopic Ratio
0-1	0.00	0.0388
2F	1.99	0.1173
4F	4.33	0.2018
6F	6.53	0.2651
8F	8.14	0.3278
10F	10.16	0.4368
12F	12.02	0.4829
14F	14.17	0.5339
16F	16.20	0.6184
18F	18.04	0.6660
20F	20.27	0.7341
22F	21.82	0.7872
24F	24.16	0.8454

Figure 1: Best fit curve (Equation 1) for 0 to 24 Mrad standard graph using Perkin - Elmer, Model 1430 spectrophotometer

The standard graph was then constructed and compared against similar data compiled on the Perkin - Elmer Model 1640 FT - IR used to do the on-line monitoring. As can be seen in Figure 2, there is very close correlation between the two instruments.

Figure 2: Data correlation between Model 1430 grating and Model 1640 FT-IR spectrophotometer

The standard, tertiary dosimeter curve for doses ranging from 0 to 100 Mrads was constructed in similar manner. By calibrating against the secondary dosimeters and extending the dose range to 100 Mrads, there was only a slight shift in the data. The best fit curve of the standard graph, Figure 3, resulted in the following equation.

$$\text{Dose (Mrad)} = 7.05\text{Sr}^2 + 25.29\text{Sr} - 2.59 \quad (2)$$

As can be seen in the graph, there is good correlation down to a spectroscopic ratio of 0.9. Therefore, both equations were used in the computer

program; Equation (1) was used for spectroscopic ratios less than 0.9 and equation (2) for spectroscopic ratios greater than 0.9.

Figure 3: 0 to 100 Mrad standard graph using Perkin - Elmer 1430 spectrophotometer.

An "OBEY" program (See Appendix 1) was then written with commands to run the Model 1430 spectrometer between the wave frequencies of 2200 and 1900 cm^{-1} and 1020 and 920 cm^{-1} , to direct the user in collecting data points at the I and I_0 frequencies, to calculate the spectroscopic ratio using Beer's law and to convert the spectroscopic ratio to beam dose using the above two equations for the standard graph. With this program the beam dose of each slab was determined by measuring the dose of each dosimeter attached to that slab.

Spectral scans were then attempted on the 20 mil thick slabs exposed to 80 Mrads dose. It became immediately apparent that although a slab of this thickness was desirable for dosimetry work, it was too thick for this study which included examination of the EVA and EEA copolymers and their blends. The carbonyl bands became too broad and intense to resolve the ketone bands (1710 cm^{-1}). Therefore, thinner films were pressed from all 80 Mrad dosed slabs of each blend representing all three types of irradiation. In addition, films were pressed from each uncrosslinked and each chemically crosslinked blend. All films were pressed to 7.7 ± 0.1 mil thickness and measured with a calibrated micrometer.

Spectral scans were taken of all samples from 4000 to 450 cm^{-1} and saved on disks. Absorption peaks were then measured on each spectrum between the regions of 1020 and 780 cm^{-1} for trans-vinylene, 1750 and 1550 cm^{-1} for ketone carbonyl, and 2200 and 1900 cm^{-1} for "thickness" by selecting the I and I_0 values to determine the peak's absorbance. Best resolution of the ketone carbonyl and trans-vinylene peaks in the copolymer and copolymer blended samples was obtained with spectral subtraction of the uncrosslinked sample of like formulation. The ratio of the absorbance of these peaks to the "thickness" peak was calculated and plotted for comparison.

Similar work was done on a series of xylene extracted samples. The soluble fractions were cast onto a NaCl crystal and examined first for the presence of the carbonyl and trans-vinylene bands and second for a comparison of these ratios to those of the pressed film samples.

2.4c Solid State FT-NMR Spectroscopy

Two ^{13}C solid state NMR experiments were conducted on HDPE #1 samples only. For these experiments, two grams each of the ^{60}Co 80 Mrad irradiated, the electron irradiated 80 Mrad, the chemically crosslinked and the uncrosslinked raw polymer were cryogenically ground to a powder using a SPEX Model 6700 Freezer/Mill.

The first experiment was conducted at room temperature using the Bruker MSL-300 NMR operating at 75.47 MHz for carbon. Solid state NMR spectra were acquired on powdered samples using magic-angle spinning with cross polarization (CP/MAS). High powered decoupling was implemented during acquisition to eliminate dipolar interaction. All samples were spun at rates sufficiently fast, 5 kHz, to remove spinning side bands. The 90° pulse length was $4\mu\text{sec}$. Sixteen scans were collected for each spectrum at a rate of repetition of 5 seconds/scan. All ^{13}C chemical shifts were referenced to glycine.

A second experiment, also at room temperature, was conducted using a Chemagnetics CMX-200 NMR operating at 50.27 MHz for detection of ^{13}C . This experiment required a single pulse with decoupling during acquisition. Magic angle spinning was carried out at a rate of 3.5 kHz. The 90° pulse length was $5.5\mu\text{sec}$. with acquisition delayed 500 msec., 5 sec., and 60 seconds for each sample tested. One hundred scans were collected for each spectrum. The chemical shifts relative to tetramethylsilane (TMS) were determined from the aromatic peak at 132.3 ppm in hexamethylbenzene (HMB). To assure there were no significant changes as a result of the instrumental differences, the above 75.47 MHz CP/MAS experiment was repeated on two of the samples under similar conditions. They too were referenced to HMB.

Figure 4: NMR experimental timing diagrams

The pulse sequences used are schematically shown in Figure 4. Pulse sequence I is used to obtain ^{13}C spectra with cross polarization. This sequence allows one to see the spectrum as related to proton relaxation. Pulse sequence II, with a single pulse allows one to look at the carbon relaxation. A short time delay permits sufficient time for relaxation of unrestrained carbons residing in the amorphous phase, but not in the crystalline phase of the polymer. Increased time delay permits sufficient time for relaxation of those carbons restrained within the crystalline phase.

2.4d DSC Procedure

Samples for differential scanning calorimetry (DSC) were cut from the pressed slabs of blended and crosslinked material to be as close to 9.0 milligrams as possible. All DSC measurements were done using a Perkin - Elmer DSC-7 interfaced with a 7700 data station. The instrument calibration was checked daily before use with an indium standard for the melting point of 156.6°C. Recalibration with indium and lead (melting point = 327.5°C) was conducted whenever the indium standard showed a melt temperature which deviated from 156.6° by greater than 0.2°C. In addition, prior to conducting any sample runs, the baseline was calibrated to provide as flat and uniform a line as possible. A blank was then run and saved in the memory for later use.

DSC scans were conducted on all samples representing the highest level of crosslinking for each blend and method of crosslinking. In addition, scans were conducted on all uncrosslinked materials and blends for reference, and on all dose levels for the HDPE #1 sample for the purpose of observing trends. All DSC experiments consisted of three cycles: a heat cycle, a cool cycle and a second heat cycle. The total experiment was conducted at a 10°C per minute temperature scan rate between 40° and 150°C with a five minute hold time at 150°C after the first heat cycle and another five minute hold time at 40°C after the cool cycle. All cycles were conducted with a continuous nitrogen purge. The previously saved blank scan was then automatically retrieved from the computer memory and subtracted from the sample scan to compensate for any baseline effects. The recrystallization exotherm (T_c) during the cooling cycle, the melting endotherm (T_m) and the heat of transition (ΔH) during the second heat cycle were recorded.

The first heat cycle where the sample is taken above its melt temperature and held for five minutes is designed to assure total melt of the sample and elimination of its previous thermal history. A 10°C per minute cool rate to 40°C with a hold time of five minutes then establishes a controlled, reproducible recrystallization history for all samples with time for stabilization prior to the second heat cycle.

RESULTS AND DISCUSSION

Chemical or radiation induced crosslinking and chain scission are irreversible chemical processes which result in a change in the physical and chemical structure of polymers. Crosslinking proceeds via formation of chemical bonds inter- and intramolecularly. In this process the molecular weight of the polymer increases and a three dimensional network is established. Chain scission results from a cleavage of the backbone as well as from severance of the side groups from the polymer molecule. As a rule, crosslinking and chain scission proceed simultaneously, but the efficiency of each can be quite different depending upon many factors such as: the chemical structures of the macromolecule, the polymer structure, the method of polymer production and the method of crosslinking or irradiation (26).

Oxygen dissolved in polymeric materials is a factor which significantly affects their radiation resistance. Its presence results in chain scission and the formation of oxygen containing functional groups. Radiation induced free radicals resulting from hydrogen atom abstraction initiate the previously discussed chain reactions (p 5) which progress from a free radical to a peroxy radical to the carbonyl functional group (RCO). The rate and direction of RCO formation depends on the chemical structure of the polymer, the oxygen concentration and the radiation parameters, such as dose, dose rate and type of irradiation (26). The higher the dose and the lower the dose rate at the same total dose, the greater the formation of peroxide crosslinks which decompose (20). The oxidation reaction can be kinetically or diffusion controlled, depending on the ratio of oxygen input to its consumption. When the rate of oxygen consumption is higher than dissolution, one observes diffusion controlled reactions. Therefore, the method of irradiation used for crosslinking the polymer and the availability of oxygen during the irradiation are key factors which will affect the increase in molecular weight relative to the dose provided.

The irreversible radiation-induced changes in the thermal characteristics of polymeric materials usually originate in structural transformation resulting in

crosslinking. The most important factor for semicrystalline polymers is the change in crystallinity (26). Heat of fusion, which is a measure of crystallinity, is controlled by the chemical structure of the polymer. These important inter- and intramolecular structure characteristics include structural regularity, bond flexibility, close packing and inter chain attraction. In general, high melting points are associated with highly regular structures, rigid molecules, close packing capability, strong inter chain attraction, or several of these factors combined (27). Since, crosslinking creates structural irregularities and affects molecular packing, it is not surprising that changes have been observed in both the degree of crystallinity (10) and the melting point (14) of polyethylene relative to dose exposure.

3.1 Percent Gel

At a certain density of intermolecular bonds, the polymer becomes insoluble in solvents to form the gel fraction. For polyethylene based polymers, the solvent of choice is xylene. The minimum absorbed dose of radiation at which the insoluble fraction appears is called the gel dose. Crosslinking results in a change in the molecular weight distribution of the polymer. Therefore, data on crosslinking can be obtained by measuring the characteristic solubility of the irradiated polymer.

Polyethylene and ethylene based copolymers such as EVA and EEA preferentially tend toward crosslinking rather than chain cleavage. Therefore, with progressively increased radiation, molecular weight increases and the solubility of these polymers decreases once the gel dose is surpassed.

Because of the competing reactions which occur during crosslinking and irradiation, measurement of the gel fraction can be a means of determining the efficiency of a crosslinking method. If irradiation creates free radicals in an oxygen free environment, there is a far greater tendency for that radical to react with another free radical forming either a vinyl group or a crosslink. If a crosslink forms, there will be increased molecular weight and proportionally increased gel. However, if oxygen is present, there are two factors which result

in a decreased efficiency in gel formation. The first is that fewer free radicals will be available for formation of crosslinks due to their consumption through reaction with oxygen. The second is that radicals reacting with oxygen ultimately lead to chain scission. This negates some of the increased molecular weight caused by crosslinking.

In this study, the percent gel was determined in all polymers and blends with copolymers for each dose level and each crosslinking technique. The greatest emphasis was placed on the electron irradiated and ^{60}Co irradiated in N_2 samples because they were thought to be the most difficult to differentiate. Thus, because of the Co beam capacity limitations, only two dose levels were applied to the ^{60}Co in air series. The gel data for each crosslinking method is given in tables VII through XVI for their respective blends. The reproducibility of these values varied depending on the exposure dose. Samples of low dose, 10 Mrads or less, had a range in percent gel data 0.1 % to 3.7 % with an average of 1.5 %. Samples greater than 10 Mrads had a range from 0.0 % to 3.0 % with an average of 0.6 %. Wider data spread in the low dose samples is due to the lack of formation of a significant three dimensional network. With the absence of a well established network, portions of gel can pass through the gauze or screen (see experimental) leading to decreased precision. Therefore, the lower the percent gel, the less precise the gel data.

Although the difference in crosslinking efficiency between ^{60}Co in N_2 and electron irradiated polymers at most doses is rather subtle, a consistency does exist. All ten polymers or polymer blends graphed in figures 5 - 14 display a decrease in percent gel with increased oxygen exposure or decreased dose rate. Crosslinking by ^{60}Co in N_2 is a slow process, but only the oxygen dissolved in the polymer is available for the oxidation side reaction. After the oxygen is consumed, crosslinking is kinetically controlled by this radiation technique. Therefore, it is the most efficient in forming crosslinks.

Conversely, crosslinking by electron beam and ^{60}Co in air are less efficient due to of the continuous oxygen input and its consumption ratio. Because the ^{60}Co irradiation process is almost three orders of magnitude

slower than the electron beam, there is a substantial increase in time for oxygen diffusion to cause a decrease in crosslinking efficiency. Therefore, because the formation of crosslinks by ^{60}Co in air irradiation are more diffusion controlled, this crosslinking technique is the least efficient.

At a 10 Mrad exposure dose, the decreased efficiency is not as obvious, especially in the HDPE and HDPE blends. But, what is more important is that at 10 Mrads or less, the gel level seldom exceeds 30% in the HDPE formulations. This can be explained by the fact that HDPE's are more crystalline and have available less amorphous phase in which the crosslinking occurs to form a network. Therefore, with less precise data from incomplete network formation, it is more difficult to make consistent distinctions between the crosslinking method. However, the distinction becomes very clear and pronounced at the higher dose levels. Figures 13 and 14 with gel data at all doses with all three irradiation methods show clear distinctions with doses of 20 Mrads or higher.

The last table of the series (Table XVII) lists only the gel data for the chemically crosslinked polymers. This data cannot be compared on the same graphs with the irradiated polymers because there is no way of making a dose comparison. But, what is evident is that 2% Dicumyl peroxide provides gel levels comparable to those produced by an 80 Mrad dose. Therefore, since the crosslink density of the chemically crosslinked polymers is similar to that of the 80 Mrad beamed samples, most future comparisons between the chemically crosslinked and irradiated polymers will be made at 80 Mrad dose levels.

Table VII: Percent gel of HDPE #1 at varied dose levels.

X-link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	0.46	10.55	44.03	64.52	77.11
Co in N ₂	0.14	27.46	57.55	74.09	83.39
Co in Air		17.92			66.71

Figure 5: Percent gel comparison of HDPE #1 using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table VIII: Percent gel of LDPE #1 at varied dose levels.

X-link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	0.38	23.25	50.18	71.47	83.14
Co in N ₂	0.24	28.59	58.19	77.48	89.00
Co in Air		14.15			57.51

Figure 6: Percent gel comparison of LDPE #1 using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table IX: Percent gel of HDPE #1/EVA at varied does levels.

X-link Type	% Gel at Varied dose				
	5	10	20	40	80
Electron Beam	10.05	23.55	54.85	73.89	82.40
Co in N ₂	25.90	42.67	67.10	80.06	88.75
Co in Air		20.64			53.48

Figure 7: Percent gel comparison of the HDPE #1/EVA blend using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table X: Percent gel of HDPE #1/EEA blend at varied dose levels.

X-link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	9.95	27.29	54.25	72.37	82.52
Co in N ₂	30.22	45.78	67.03	80.45	89.17
Co in Air		20.79			53.36

Figure 8: Percent gel comparison of the HDPE #1/EEA blend using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table XI: Percent gel of LDPE #1/EVA blend at varied dose levels.

X-link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	15.47	42.88	74.16	85.20	90.75
Co in N ₂	28.71	63.61	83.76	89.08	94.87
Co in Air		23.82			51.67

Figure 9: Percent gel comparison of the LDPE #1/EVA blend using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table XII: Percent gel of LDPE #1/EEA blend at varied dose levels.

X-Link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	6.49	31.34	58.59	76.97	86.01
Co in N ₂	24.31	49.47	71.61	83.69	91.83
Co in Air		16.38			41.81

Figure 10: Percent gel comparison of the LDPE #1/EEA blend using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table XIII: Percent gel of EVA at varied dose levels.

X-Link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	28.29	57.07	77.00	87.21	92.90
Co in N ₂	51.69	75.19	85.92	92.61	96.15
Co in Air					59.51

Figure 11: Percent gel comparison of EVA using electron beam, ^{60}Co in N₂, and ^{60}Co in air at varied dose levels.

Table XIV: Percent gel of EEA at varied dose levels.

X-Link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	4.07	44.85	68.23	81.58	89.52
Co in N ₂	51.55	71.41	80.51	89.29	93.43
Co in Air					52.30

Figure 12: Percent gel comparison of EEA using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table XV: Percent gel of HDPE #2 at varied dose levels.

X-link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	4.35	31.38	56.15	74.02	83.85
Co in N ₂	8.47	41.16	68.58	82.05	89.87
Co in Air	4.07	28.27	47.44	56.01	70.28

Figure 13: Percent gel comparison of HDPE #2 using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table XVI: Percent gel of LDPE #2 at varied dose levels.

X-link Type	% Gel at Varied Dose				
	5	10	20	40	80
Electron Beam	21.10	44.38	62.71	75.08	84.17
Co in N ₂	40.48	59.02	74.29	82.60	88.32
Co in Air	11.81	28.19	39.25	42.62	49.30

Figure 14: Percent gel comparison of LDPE #2 using electron beam, ⁶⁰Co in N₂, and ⁶⁰Co in air at varied dose levels.

Table XVII: Percent gel of chemically crosslinked polymer formulations cured 10 min. at 195°C.

Sample	Run #1 % Gel	Run #2 % Gel	Average % Gel	Range Δ (%)
HDPE #1	93.33	95.84	94.59	2.51
LDPE #1	69.35	70.64	70.00	1.29
HDPE #1/EVA	93.19	94.24	93.72	1.05
HDPE #1/EEA	89.46	89.74	89.60	0.28
LDPE #1/EVA	86.73	84.92	85.83	1.81
LDPE #1/EEA	80.69	80.97	80.83	0.28
EVA	93.80	94.28	94.04	0.48
EEA	89.74	90.32	90.03	0.58

3.2 Infrared Spectroscopy

Measuring chemical changes is difficult to observe within crosslinked polymers because of their insolubility. In addition, since the major physical changes take place below 100 Mrads dose, only low doses will be used for most industrial applications. Therefore, the chemical changes which do occur will be quite small (10).

Aside from crosslinking, the most noticeable change which occurs is an increase in the main chain unsaturation. Although much work has been done using bromine and iodine uptake, this study will be confined to infrared analysis of irradiated films. Three main spectral bands related to unsaturation are: trans-vinylene, terminal vinyl, and terminal methyl at 965, 909, and 890 cm^{-1} respectively. The latter two correspond to pendent groups at the end of or along the chain, while trans-vinylene unsaturation occurs within the main chain when two adjacent hydrogen atoms are removed. Measurement of this band as well as the ketone carbonyl previously discussed, relative to oxidation, are the major focus of this study.

To assure all samples had received adequate radiation exposure, the dosimeters attached to each sample were measured and recorded. Tables XVIII through XX list the results. Tables XVIII and XIX show consistent dose levels for most readings within 5% of the desired exposure. There are a few exceptions with as much as a 10% deviation at the 5 Mrad dose levels. The EVA and EEA samples for 80 Mrad ^{60}Co dose appear to be 20 Mrads too low. Since an EVA and an EEA slab was observed on the lab counter during a term when other samples were being exposed to a 20 Mrad dose, it is the author's opinion that these two samples did not receive the full 80 Mrad dose. Table XX shows a dramatic reduction in the received dose due to exposure in the presence of air. However, the samples from Table XIX which were simultaneously exposed while in a nitrogen atmosphere verify that adequate exposure was provided.

Comparisons were made between crosslinked and uncrosslinked samples at 80 Mrads dose to identify the spectral regions where change

Table XVIII: Electron beam dose measurements taken from dosimeters attached to each sample. Each recorded measurement is an average of the readings taken in the machine and transverse direction.

Sample	Electron Beam Dose Levels				
	5 Mrads	10 Mrads	20 Mrads	40 Mrads	80 Mrads
HDPE #1	4.88	9.83	20.46	40.48	78.22
LDPE #1	4.61	9.78	20.70	39.28	78.18
HDPE #1/EVA	4.82	9.87	20.52	40.13	79.88
HDPE #1/EEA	4.78	9.67	20.52	40.73	79.29
LDPE #1/EVA	4.90	10.06	20.06	40.71	79.31
LDPE #1/EEA	4.73	9.83	20.55	40.18	79.50
EVA	4.81	9.91	20.43	35.70	75.72
EEA	4.82	9.65	19.73	37.21	83.32
HDPE #2	4.91	9.83	19.41	39.78	78.81
LDPE #2	4.64	9.80	19.93	39.70	79.22
Average	4.79	9.82	20.23	39.39	79.15
Std. Dev.	0.10	0.12	0.43	1.65	1.88
Max.	4.91	10.06	20.70	40.73	83.32
Min.	4.61	9.65	19.41	35.70	75.72

Table XIX: ^{60}Co in N_2 dose measurements taken from dosimeters attached to each sample. Each recorded measurement is an average of the readings taken in the machine and transverse direction.

Sample	^{60}Co in N_2 Beam Dose Levels				
	5 Mrads	10 Mrads	20 Mrads	40 Mrads	80 Mrads
HDPE #1	5.31	9.98	20.01	40.59	80.83
LDPE #1	5.21	10.03	19.32	40.53	80.79
HDPE #1/EVA	5.29	9.68	18.94	39.74	81.45
HDPE #1/EEA	5.18	9.94	18.40	40.44	80.75
LDPE #1/EVA	4.99	10.01	19.84	40.25	82.09
LDPE #1/EEA	5.13	10.15	20.08	40.59	81.77
EVA	4.65	10.12	19.23	39.48	63.02
EEA	4.87	10.25	19.44	39.79	65.41
HDPE #2	5.12	10.00	19.90	39.28	80.52
LDPE #2	4.12	10.11	20.03	41.01	80.18
Average	5.08	10.02	19.41	40.18	77.01
Std. Dev.	0.23	0.17	0.57	0.44	7.94
Max.	5.31	10.25	20.08	40.59	82.09
Min.	4.65	9.68	18.40	39.48	63.02

Table XX: ^{60}Co in air dose measurements taken from dosimeters attached to each sample. Each recorded measurement is an average of the readings taken in the machine and transverse direction.

Sample	^{60}Co in Air Beam Dose Levels				
	5 Mrads	10 Mrads	20 Mrads	40 Mrads	80 Mrads
HDPE #1		8.97			57.40
LDPE #1		8.77			59.81
HDPE #1/EVA		8.72			57.15
HDPE #1/EEA		8.75			59.27
LDPE #1/EVA		8.35			55.72
LDPE #1/EEA		8.58			62.14
EVA					53.08
EEA					57.37
HDPE #2	4.91	9.25	17.27	32.97	59.62
LDPE #2	4.64	8.89	18.40	34.10	63.27
Average	4.78	8.79	17.84	33.54	58.48
Std. Dev.	0.19	0.27	0.80	0.80	3.00
Max.	4.91	9.25	18.40	34.10	63.27
Min.	4.64	8.35	17.27	32.97	53.08

occurred and to determine whether those changes were sufficiently significant for reliable measurement. Clearly, the regions of greatest spectral change are those of the ketone carbonyl (1710 cm^{-1}) from oxidation and the trans-vinylene (965 cm^{-1}) from main chain unsaturation. These differences can be observed in the spectrum below, Figure 15. Both the bands are significant and measurable. In fact, the ketone carbonyl band is far more intense than expected. In addition to seeing the presence of the trans-vinylene band, we can see a disappearance of the terminal vinyl peaks from the uncrosslinked sample at 909 and 991 cm^{-1} . Therefore, the two major spectral ranges of interest will be from 2200 to 1550 cm^{-1} and 1200 to 800 cm^{-1} . No other chemical changes are evident from the spectra.

Figures 16 and 17 show an obvious increase in intensity of both the carbonyl and trans-vinylene bands relative to increased dose. Figure 16 was plotted as multiple overlays with no offset to display not only the increased intensity of the carbonyl band relative to the increased dose, but also the

Figure 15: HDPE #1, comparison of uncrosslinked control (a) to 80 Mrad electron beam irradiated slab (b).

Figure 16: Increased absorption of ketone carbonyl band (1710 cm^{-1}) in HDPE #1 relative to increased electron beam irradiation. Black, purple, brown, green, blue, and red representing 0, 5, 10, 20, 40, and 80 Mrads dose respectively from the electron beam.

Figure 17: Progressive growth of trans-vinylene band (965 cm^{-1}) in HDPE #1 and disappearance of terminal vinyl bands with increased electron beam irradiation. Black, purple, brown, green, blue, and red representing 0, 5, 10, 20, 40, and 80 Mrads respective dose.

consistency of the surrounding absorption bands. The one band of particular interest is at 2020 cm^{-1} , which was previously identified as being related to the crystalline region of the polymer. Throughout the remainder of this report, it will be referred to as the "thickness" peak. The thickness peak is the one against which both the trans-vinylene and ketone carbonyl will be measured to determine the spectroscopic ratio values. It will serve as a means of normalizing any peak intensity differences caused by varied film thickness.

Since the changes in absorption bands, particularly the carbonyl, were significant in the high and low density polyethylenes, the next step was to determine whether these bands would be masked with the addition of EVA or EEA. As is seen in the worst case with EVA in Figure 18 below, this is a problem. Both the ketone carbonyl and the trans-vinylene bands are masked by the carbonyl and C-O-C linkages respectively from the EVA copolymer. But, by conducting spectral subtraction of the uncrosslinked copolymer from the

Figure 18: 80 Mrad electron beam irradiated HDPE #1/EVA blend.

Figure 19: Remaining ketone carbonyl after spectral subtraction of HDPE #1/EVA control from 80 Mrad irradiated HDPE #1/EVA blend.

Figure 20: Remaining trans-vinylene band after spectral subtraction of HDPE #1/EVA control from 80 Mrad irradiated HDPE #1/EVA blend.

spectrum of the crosslinked blend, the ketone carbonyl and the trans-vinylene bands can be more clearly resolved as seen in Figures 19 and 20.

Once the spectral regions, the peak wave numbers and the method of resolving these peaks was determined, data acquisition was relatively straight forward. Films, 7.7 mils thick, were pressed for spectra of every uncrosslinked (controls), chemically crosslinked and 80 Mrad irradiation crosslinked polymer or polymer blend. Additional films were pressed for all dose levels of the electron beam irradiated HDPE #1 and LDPE #1 samples. Spectra were collected on all films in the region of 4000 and 450 cm^{-1} . With the assistance of the "Zoom" and the "Cursor" functions, data was reproducibly collected from each spectrum of the unblended polyethylenes to within less than 0.1 percent transmittance at 1970 and 2020, 1970 and 1712, and 930 and 965 cm^{-1} wavenumbers. These points represented the baseline (I_0) and peak maxima (I) values of the thickness, ketone carbonyl and trans-vinylene peaks respectively used in calculating the spectroscopic ratio (S_r) for both the carbonyl and trans-vinylene peaks.

However, with the copolymer blends, this procedure is much more subjective. Additional factors such as peak shift, the amount of peak subtraction and band broadening must be considered when spectral subtraction was conducted. Effects these factors had were either minimized or determined as follows. First, spectral band shifts often occur in blended materials due to molecular interaction. To minimize the effect this would have on a subtraction spectrum, a spectrum of the uncrosslinked control of identical formulation was subtracted from the spectrum of the irradiated blend. Thus, if band shifts existed, they were present in both. Second, since the control and irradiated blend were of like formulation and nearly the same film thickness, a subtraction factor of 1.0 was consistently used with an occasional need to go as high as 1.06. Variation from 1.0 would depend upon the appearance of the spectrum. Subtraction is conducted up to a point where the carbonyl band of the copolymers is no longer visible, but not to a point of negative absorbance. This amount of variation in the subtraction factor could effect a typical 4.0 S_r value by as much as 5%. Finally, band broadening occurs with oxidation. As a result, perfect spectral subtraction can never be made by subtracting the spectrum of

an unoxidized sample from an oxidized one. This effect is apparent in Figure 19. The sharp spike at 1715 cm^{-1} is a residual portion of the broadened carbonyl band which was not subtracted. The slightly weaker, rounded peak at 1710 cm^{-1} is the ketone carbonyl that is to be measured. Although spectral subtraction is more subjective, the ultimate effect on the S_r values can be held to less than 5% if it is conducted with consistency and caution.

All collected data was recorded and tabulated in Tables XXI through XXV. Included with the data are the calculated values for the S_r of the ketone carbonyl and trans-vinylene peaks. In order to more clearly observe trends in these ratio values, Figures 21 and 22 were made to compare the S_r for each polymer or blend with the crosslinking method used. For the trans-vinylene S_r data, Figure 21, there is a very clear distinction between the chemically crosslinked and the radiation crosslinked polymers. No further distinction can be made. However, in Figure 22, not only is the S_r for the ketone carbonyl of all the chemically crosslinked polymers distinguishably lower than the S_r for all other methods of crosslinking: but also, the S_r values for those samples irradiated in air by ^{60}Co are almost always sufficiently high to provide a means of identifying this irradiation method.

This tendency toward high ketone carbonyl S_r data implies that identifying polymers irradiated in air by ^{60}Co might be possible if there is a straight forward means of enhancing the data. One way would be to divide the S_r for the carbonyl by the percent gel. Since the percent gel, discussed in the previous experiments, tended toward being lower for polymers irradiated in air, this ratio could create sufficient separation to provide a clearer domain of data. The result of taking the S_r of the ketone carbonyl from Tables XXI through XXV, dividing them by the percent gel recorded in Tables VII through XVI, multiplying by 100 and plotting against the S_r for trans-vinylene is graphically displayed in Figure 23. Also, to have some idea of where lower dose samples would lie, data from Table XXV for HDPE #1 and LDPE #1 were included.

A very distinct cluster of data points representing the chemically crosslinked polymers exists in Figure 23. In addition, with the exception of one data point, a second cluster exists representing polymers irradiated by ^{60}Co in air. However, there is no distinction that can be made between polymers irradiated by ^{60}Co in N_2 and electron beam.

80 Mr Electron Beam

Sample	Thickness		Trans-vinylene		Carbonyl		Sr Trans- vinylene	Sr Ketone Carbonyl
	(%T) max @ 1970cm ⁻¹	(%T) min @ 2020cm ⁻¹	(%T) max @ 930 cm ⁻¹	(%T) min @ 965 cm ⁻¹	(%T) max @ 1970cm ⁻¹	(%T) min @ 1712cm ⁻¹		
HDPE #1	90.93	70.06	79.11	59.54	90.93	29.85	1.0899	4.2721
LDPE #1	94.99	72.55	83.68	59.89	94.99	74.08	1.2412	0.9226
HDPE #1/EVA	97.48	71.14	98.91	68.69	97.48	32.13	1.1575	3.5234
HDPE #1/EEA	99.55	72.97	88.14	58.40	99.55	34.40	1.3252	3.4210
LDPE #1/EVA	94.23	75.39	89.83	66.49	94.23	45.42	1.3488	3.2716
LDPE #1/EEA	95.50	75.18	94.17	65.64	95.50	40.07	1.5086	3.6302
EVA	95.97	81.02	86.77	56.91	95.97	40.99	2.4908	5.0237
EEA	91.27	71.25	93.39	63.07	91.27	39.12	1.5852	3.4212
HDPE #2	91.94	68.85	84.28	61.10	93.91	58.92	1.1121	1.6118
LDPE #2	92.08	72.54	76.37	51.90	93.49	73.10	1.6195	1.0315

Table XXI: Infrared spectroscopy data for 80 Mrad electron beam irradiated polymers.

80 Mr Cobalt in Nitrogen

Sample	Thickness		Trans-vinylene		Carbonyl		Sr Trans- vinylene	Sr Ketone Carbonyl
	(%T) max @ 1970cm ⁻¹	(%T) min @ 2020cm ⁻¹	(%T) max @ 930 cm ⁻¹	(%T) min @ 965 cm ⁻¹	(%T) max @ 1970cm ⁻¹	(%T) min @ 1712cm ⁻¹		
HDPE #1	90.86	68.61	71.13	50.03	90.86	25.12	1.2528	4.5772
LDPE #1	93.05	69.44	80.40	55.95	93.05	68.70	1.2388	1.0366
HDPE #1/EVA	93.73	70.07	98.99	70.01	93.73	25.90	1.1906	4.4210
HDPE #1/EEA	96.55	70.11	68.93	47.78	96.55	23.58	1.1453	4.4053
LDPE #1/EVA	94.86	72.68	95.09	64.88	94.86	37.43	1.4353	3.4916
LDPE #1/EEA	97.85	73.80	90.69	63.32	97.85	38.77	1.2736	3.2820
EVA	96.32	75.58	86.11	59.01	96.32	40.69	1.5585	3.5536
EEA	96.42	78.65	93.66	72.18	96.42	36.49	1.2788	4.7700
HDPE #2	90.46	66.52	85.11	56.87	90.46	50.47	1.3115	1.8982
LDPE #2	89.54	66.48	72.98	48.45	89.54	72.05	1.3757	0.7298

Table XXII: Infrared spectroscopy data for 80 Mrad ⁶⁰Co irradiated polymers in nitrogen.

80 Mr Cobalt in Air

Sample	Thickness		Trans-vinylene		Carbonyl		Sr Trans- vinylene	Sr Ketone Carbonyl
	(%T) max @ 1970cm ⁻¹	(%T) min @ 2020cm ⁻¹	(%T) max @ 930 cm ⁻¹	(%T) min @ 965 cm ⁻¹	(%T) max @ 1970cm ⁻¹	(%T) min @ 1712cm ⁻¹		
HDPE #1	98.22	74.63	73.26	52.11	98.22	4.24	1.2403	11.4416
LDPE #1	93.60	73.72	72.54	52.37	94.31	23.39	1.3646	5.8398
HDPE #1/EVA	94.01	74.67	89.89	65.69	94.01	16.90	1.3617	7.4508
HDPE #1/EEA	98.51	77.04	87.78	66.40	98.51	18.49	1.1355	6.8051
LDPE #1/EVA	94.08	78.47	92.44	71.89	94.01	30.58	1.3858	6.1900
LDPE #1/EEA	97.67	80.28	80.90	63.00	97.67	23.28	1.2754	7.3136
HDPE #2	92.19	68.02	79.38	53.65	93.84	23.47	1.2885	4.5580
LDPE #2	96.19	77.49	62.72	47.55	96.19	4.28	1.2805	14.3974

Table XXIII: Infrared spectroscopy data for 80 Mrad ⁶⁰Co irradiated polymers in air.

Chemically Crosslinked

Sample	Thickness		Trans-vinylene		Carbonyl		Sr Trans- vinylene	Sr Ketone Carbonyl
	(%T) max @ 1970cm	(%T) min @ 2020cm ⁻¹	(%T) max @ 930 cm ⁻¹	(%T) min @ 965 cm ⁻¹	(%T) max @ 1970cm ⁻¹	(%T) min @ 1712cm ⁻¹		
HDPE #1	93.16	67.22	89.11	84.92	93.16	88.15	0.1476	0.1694
LDPE #1	91.93	66.25	84.53	80.43	91.93	86.39	0.1518	0.1897
HDPE #1/EVA	95.62	71.93	94.34	87.80	95.62	79.90	0.2524	0.6309
HDPE #1/EEA	94.74	68.98	92.68	88.09	94.74	87.52	0.1601	0.2498
LDPE #1/EVA	95.63	81.59	85.34	81.68	95.63	89.43	0.2761	0.4222
LDPE #1/EEA	93.67	70.19	95.34	90.95	87.90	78.46	0.1634	0.3937
EVA	98.81	80.61	77.67	72.06	98.81	90.42	0.3683	0.4359
EEA	99.40	75.94	93.69	86.44	90.85	78.88	0.2992	0.5248

Table XXIV: Infrared spectroscopy data for Dicumyl peroxide cured polymers.

Electron Beam

Sample	Thickness		Trans-vinylene		Carbonyl		S _r Trans- vinylene	S _r Ketone Carbonyl
	(%T) max @ 1970cm ⁻¹	(%T) min @ 2020cm ⁻¹	(%T) max @ 930 cm ⁻¹	(%T) min @ 965 cm ⁻¹	(%T) max @ 1970cm ⁻¹	(%T) min @ 1712cm ⁻¹		
HDPE #1 (5 Mr)	94.83	72.69	89.28	84.11	94.83	79.65	0.22	0.66
HDPE #1 (10 Mr)	94.14	72.63	87.40	79.73	94.14	65.52	0.35	1.40
HDPE #1 (20 Mr)	94.92	73.32	86.93	74.77	94.14	59.13	0.58	1.80
HDPE #1 (40 Mr)	90.95	68.61	79.77	64.90	90.95	39.34	0.73	2.97
LDPE #1 (5 Mr)	94.26	69.67	89.91	84.61	94.26	78.92	0.20	0.59
LDPE #1 (10 Mr)	94.59	70.81	89.46	81.75	94.59	66.82	0.31	1.20
LDPE #1 (20 Mr)	91.70	69.47	84.70	72.81	91.70	53.65	0.54	1.93
LDPE #1 (40 Mr)	91.61	69.15	78.23	63.08	91.61	31.89	0.77	3.75

Table XXV: Infrared spectroscopy data for 5, 10, 20, and 40 Mrad electron beam irradiated HDPE #1 and LDPE #1.

Figure 21: Spectroscopic ratio of trans-vinylene for all blends comparing the four crosslinking methods.

Figure 22: Spectroscopic ratio of the ketone carbonyl for all blends comparing the four crosslinking methods.

Figure 23: Two dimensional plot for separating crosslinked polymers into classes based on crosslinking method.

Figure 24: Two dimensional plot (%Gel vs. S_r) for separating crosslinked polymers into classes based on crosslinking method.

Because of the many polymer additives such as plasticizers, stabilizers and flame retardants, the S_r values for the ketone carbonyl band may not always be attainable. Therefore, Figure 24 is a plot of percent gel vs. the S_r of trans-vinylene. This graph likewise shows a very clearly separated cluster of data points representing the chemically crosslinked polymers. But, quite surprisingly, it also shows a more distinct cluster of data points representing the polymers irradiated by ^{60}Co in air than the separation observed in Figure 23.

Although Figures 23 and 24 display excellent potential for separating the four methods of crosslinking into three classes of data, it must be understood that this data only represents a small population of what could exist. First, the majority of all irradiated samples are at 80 Mrad dose levels. There is high probability that with a higher population of samples with low dose levels, the polymers irradiated by ^{60}Co in air will not form as distinguishable a cluster, such as the one displayed in Figure 24. Second, although Dicumyl peroxide is often a first choice peroxide because of its favorable cure temperature, these data points represent only one chemical curing agent at one concentration. To have greater confidence in the separation boundaries would require additional testing in the above mentioned areas.

However, based upon the data collected so far, we can visually perceive a linear boundary separating the chemically crosslinked polymers from the irradiated polymers. Therefore, with the understanding that this boundary may have to be changed with additional data points from the same blends at lower dose and from polymers of the same class but different origins, we can draw an arbitrary line approximately equidistant from both clusters of data. Visual boundary selection is basically the same as mathematically determining the linear discriminate. The basic difference is that visually the whole picture is observed at once, where as mathematically, the linear discriminate is determined through an iterative process involving a point-by-point examination. The equation for the selected boundary is:

$$y = 100(x) + 25$$

Where y represents the percent gel and x is the S_r of trans-vinylene. With this equation representing the dashed line in Figure 24, we can say that whenever the S_r of trans-vinylene is greater than 0.75, the polymer has been irradiated. But, if the S_r is less than 0.75, then the sample is chemically crosslinked only if the percent gel is greater than 100 times the S_r plus 25.

Solvent extraction is a common method used for aiding in spectral analysis of filled, non-transparent, crosslinked polymers. Carbon black is a frequently used polyethylene filler because of its ability to block UV light. But, it also makes thin film spectroscopy almost impossible. Refluxing xylene as a preferred solvent is an excellent means of extracting the low molecular weight ends of the crosslinked polymer. The higher molecular weight crosslinked network is insoluble with the majority of the carbon black entrapped in the network. But, since the solvent soluble portion of the polymer is fractionally removed from the bulk polymer, one must consider how this step will effect the S_r values.

Each formulation irradiated to 80 Mrads by an electron beam was extracted with xylene and cast onto a polished salt plate for spectral examination. All data was recorded in a manner similar to the pressed films. The results are listed in Table XXVI. The S_r values for the trans-vinylene are within the same range of values as previously tested with pressed films. However, the S_r values for the ketone carbonyl are very inconsistent. But, all are greater than the S_r values for the slabs irradiated by electron beam and by ^{60}Co in N_2 . In addition, most are greater than the slabs irradiated by ^{60}Co in air. A likely explanation for this is that when reaction with oxygen occurs it ultimately leads to chain scission. These lower molecular weight segments which have reacted with oxygen and broken off from the main chain then become extracted by the solvent. Therefore, a higher concentration exists in the solvent extract.

80 Mr Electron Beam
(xylene Extract)

Sample	Thickness		Trans-vinylene		Carbonyl		Sr Trans- vinylene	Sr Ketone Carbonyl
	(%T) max @ 1970cm ⁻¹	(%T) min @ 2020cm ⁻¹	(%T) max @ 930 cm ⁻¹	(%T) min @ 965 cm ⁻¹	(%T) max @ 1970cm ⁻¹	(%T) min @ 1712cm ⁻¹		
HDPE #1	93.59	90.79	96.70	93.21	93.59	69.99	1.2102	9.5663
LDPE #1	93.87	91.02	94.56	90.81	93.87	85.91	1.3125	2.8740
HDPE #1/EVA	96.24	92.08	83.48	78.67	96.24	34.96	1.3430	22.9170
HDPE #1/EEA	93.27	89.39	93.41	88.12	93.27	39.94	1.3721	19.9606
LDPE #1/EVA	94.00	91.83	95.20	91.85	94.00	74.82	1.5338	9.7710
LDPE #1/EEA	94.21	91.22	95.88	91.56	94.21	71.22	1.4295	8.6739
EVA	97.73	96.52	93.38	91.46	97.73	71.77	1.6676	24.7820
EEA	96.62	94.46	91.97	88.60	96.62	70.07	1.6511	14.2106

Table XXVI: Infrared spectroscopy data for xylene extracts of 80 Mrad electron beam irradiated polymers and polymer blends.

3.3 Solid State ^{13}C FT-NMR

High resolution NMR spectroscopy of solid samples is a relatively new analytical technique due to a combination of the discovery of the Cross Polarization - Magic Angle Spinning (CP-MAS) method and the recent commercial availability of spectrometers for solid-state, high resolution ^{13}C NMR. This method has been used for studies on crosslinking induced by γ - irradiation of solids (28,29) for which conventional high-resolution NMR is not applicable because of the insolubility of the crosslinked polymers. For these studies, dose ranges from 300 to 1000 Mrads were used. With these high doses solid-state ^{13}C NMR showed the presence of crosslinks in polyethylene and evidence for preferential formation of radicals in the amorphous phase.

However, for most practical applications, dose levels greater than 80 Mrads would be considered excessive since the greatest changes in molecular weight, solvent solubility, heat resistance and other properties have already occurred. Therefore, a quick CP-MAS solid-state ^{13}C NMR experiment was conducted to determine what, if any, differences could be observed at dose levels of 80 Mrads or less. The four samples compared by this test were: The uncrosslinked HDPE #1 as control, the chemically crosslinked HDPE #1, the 80 Mrad irradiated HDPE #1 by ^{60}Co in N_2 , and the 80 Mrad electron beam irradiated HDPE #1.

All spectra (Figures 25 through 28) exhibit a major peak at 18.1 ppm with shoulders on each side at 19.5 and 16.6 ppm. No evidence of $\text{CH} = \text{CH}$ or COOH existed at 130 or 180 ppm respectively as was observed by J. Sohma, et al. (28) after exposing HDPE's to a 995 Mrad dose. An additional, minor peak, was observed near 0.5 ppm in the control. But, of even greater concern, the typical - CH_2 - band normally present at approximately 32.6 ppm was completely absent from all spectra.

Careful study of the spectra revealed the peaks had been right shifted approximately 15 ppm. This was concluded from Sohma's work showing the - CH_2 - band at 32.6 ppm and the - CH_3 band at 15.2 ppm. If, on the control sample (Figure 25) all peaks are shifted down field by 14.7 ppm, the peak

Figure 25: Solid-state CP-MAS ^{13}C NMR of native HDPE #1 (Control).

Figure 26: Solid-state CP-MAS ^{13}C NMR of 80 Mrad electron beamed HDPE #1.

Figure 27: Solid-state CP-MAS ^{13}C NMR of 80 Mrad irradiated HDPE #1 by Co in nitrogen.

Figure 28: Solid-state CP-MAS ^{13}C NMR of chemically crosslinked HDPE #1.

currently at 0.5 ppm would be at 15.2 ppm and the major peak at 18.2 would be at 32.8 ppm. These peak positions now correlate very well with the positions of the - CH₂ - and the - CH₃ bands described in literature.

Likewise, the two side shoulders which were originally thought to be caused by inadequate decoupling became more understandable once the peaks were shifted down field. Previous work by Kitamaru et al. correlates the two sharper peaks furthest downfield to the polymeric crystalline phase and the broader peak up field to the amorphous phase (30). If 14.7 ppm is added to the original ppm values acquired by the CP-MAS experiment, we find all peaks to be in excellent agreement with those identified by Kitamaru.

Table XXVII: CP-MAS ¹³C NMR experimental data after shifting 14.7 ppm down field compared to literature values.

Peak Position		Kitamaru Literature Data	
CP-MAS ppm	Shifted by 14.7 ppm	Location ppm	Identification
0.5	15.2	15.2	terminal methyl
16.6	31.3	31.2	amorphous
18.2	32.9	32.8	orthorhombic crystal
19.5	34.2	34.2	monoclinic crystal

For further verification of the identity of these peaks, a second single pulse solid-state MAS ¹³C NMR experiment was conducted. To better understand its purpose and how it differs from the CP-MAS experiment, we must first briefly review the cross polarization method. It is a technique used particularly with non-abundant isotopes such as ¹³C. Because of their low abundance, the distance between two ¹³C isotopes in a molecule is too great to provide sufficient dipole-dipole interactions for efficient relaxation of the ¹³C nuclei to return to the ground state. Therefore, a time lapse of several seconds

would be necessary before the sample could be pulsed again. If multiple scans are necessary to accumulate adequate signal for a spectrum, this time lapse would result in a large block of time for a single spectrum. But, the proton is a very efficient relaxer because of its abundance and freedom of motion. Cross polarization takes advantage of this fast relaxation by transferring the spin density from the protons to the ^{13}C . Under these conditions, the nuclei behave similarly and the relaxation of the weaker ^{13}C is controlled by the proton, the stronger nucleus. Therefore, most magnetization is coming from the protons.

In contrast, to verify the relationship of these peaks to the crystalline and amorphous regions of the polymer, the magnetization signal must come from the ^{13}C . By providing a single pulse to the ^{13}C , there will be no transfer of spin-density. The signal will come directly from the ^{13}C .

In semicrystalline polymers or polymer blends like polyethylene, there exist domains having different molecular mobilities such as the crystalline and amorphous phase. Magnetization signals will be based on relaxation behavior which is related to molecular mobility (31). But, because there is greater mobility in the amorphous phase, the excited nuclei will relax to ground state more rapidly than in the more restrained crystalline phase. Therefore, by designing an experiment where signal acquisition is started almost immediately after the pulse, the signal from the nuclei in the amorphous phase should predominate due to their greater freedom to relax to ground state. By incrementally extending the pulse delay, the signal from the crystalline phase should become increasingly more evident as it is allowed additional time to relax.

As can be seen in Figure 29, that is exactly what is occurring. With a 500 msec. delay, only the broad peak at 31.3 ppm representing the amorphous phase can be seen. After 5 sec. delay, the sharper peak at 32.8 ppm predominates. And after 30 seconds, both sharp peaks representing the crystalline phase are apparent with the broad amorphous peak up field as a shoulder.

Now that the identity of the three peaks has been verified, comparisons on the original spectra can be made with reasonable certainty that the

Figure 29: 80Mrad electron beamed HDPE #1 showing increased intensity of crystalline peaks with increased pulse delay: (a) 500 msec., (b) 5 sec., (c) 30 sec.

differences observed will be related to changes in crystallinity. The following table summarizes the variations in peak intensities observed in the four spectra. Each peak was measured in millimeters and calculated as a percent of the sum of the three peaks.

Table XXVIII: Comparison of crystalline vs. amorphous phase based on percent of peak height of C₁ (monoclinic), C₂ (orthorhombic), and A (amorphous).

Sample I.D.	C ₁ @ 19.55 ppm (%)	C ₂ @ 18.1 ppm (%)	A @ 17.5 ppm (%)	Crystal / Amorphous (ratio)
Control	29.28	45.48	25.23	2.96
Electron Beam(80 Mrad)	30.99	49.30	19.72	4.07
⁶⁰ Co in N ₂ (80 Mrad)	30.30	51.52	18.18	4.50
Chemical	25.71	48.10	26.19	2.82

From this experiment, three major relationships exist. First, as we have consistently seen through previous experiments, there is very little difference between samples irradiated by electron beam and ⁶⁰Co. Second, the crystalline portion of the irradiated samples has increased relative to the native control. This is in contradiction to previous x-ray diffraction work which showed that with increased radiation crosslinking there was decreased crystallinity (10). Finally, the amorphous phase of the chemically crosslinked polymer is greater than the irradiated polymers, but almost equivalent to the control. Since chemical crosslinking requires heating the sample above the melt into an amorphous state, followed by cooling after the three dimensional network has formed, one would expect this sample to have the largest amorphous phase.

Therefore, the expected progression of these four samples is that the uncrosslinked would have the greatest crystallinity and the chemically crosslinked would have the least with the irradiated samples somewhere between.

Although the data from this experiment is inconclusive, the CP-MAS method by solid-state ^{13}C NMR did show that it could have potential application in differentiating between types of crosslinking by measurement of the crystalline and amorphous phase of the polymer. But, to fully test and develop a procedure by this method would, in itself, be a comprehensive project. Thorough testing would be necessary on all blends with the varied dose levels to determine whether real trends exist. In addition, rigorous control of the sample temperature would be necessary since work by Jarrett et al. (32) reports conversion of the monoclinic crystals to orthorhombic crystals at temperatures as low as 50°C . As a result of absorbed energy during irradiation, some of these samples could have reached temperatures this high. Finally, quantitative measurement by peak height is crude at best. Far greater accuracy can be attained by deconvolution of the peaks followed by measurement of peak area. This would then have to be tested for repeatability and reproducibility.

3.4 DSC

Irradiation of polyethylene causes important modifications in the structure of the molecule such as branching, unsaturation, inter- and intramolecular bonds, that result in the geometry of the molecule being permanently altered. Since these alterations prevent the same degree of compaction and they reduced molecular mobility, the chains no longer have the same ability to orient and form regular molecular arrangements. It follows that the crystalline regions in the polymer should be greatly affected by irradiation and one can expect a gradual decrease in the degree of crystallinity with increased dose. In a like manner, it follows that the crystalline melting point should decrease since the random substitution of side branches on polyethylene lowers the melting point by as much as 25°C when going from a linear to a branched polymer (33).

Previous studies have demonstrated decreased heat of fusion (ΔH_f) and crystalline melt temperature (T_m) with increased crosslinking by both radiation (14, 34) and chemical (35) methods. Although the experiments by Luo et al. showed a 25% reduction in crystallinity due to a 1000 Mrad dose by ^{60}Co irradiation, and the work by Brenner et al. demonstrated only a 5 to 10 percent reduction in T_m and ΔH_f values with a 60 Mrad dose by electron beam, there is no information from which to make comparisons at equivalent dose levels.

In this study, numerous DSC scans were conducted first on the HDPE #1 at each of the different dose levels, and second on the uncrosslinked blends for comparison to each of the four sets of crosslinked blends: one set by chemical crosslinking and three sets by irradiation at the 80 Mrad dose level. Although some tests were done at other doses, samples of the 80 Mrad dose level are of greatest interest since their degree of crosslinking correlates more closely with the chemically cured blends.

The temperature at which these transitions occur in crystalline polymers is dependant on the heating rates. For DSC testing of polymers, 10°C per minute is an ASTM recommended rate which is a convenient compromise between a very slow rate that would induce higher crystallinity and a very fast rate where the melting point results could be shifted as much as 10°C higher. In thermoanalytical studies, it is more common to quote the melt temperature at the

intercept of the tangents to the baseline and slope maximum of the peak. However, because of the broad melting range of the polymers, all melting temperatures will be taken from the point of maximum peak height.

Figure 30 below is an overlay of two DSC scans comparing uncrosslinked with 80 Mrad electron beam irradiated LDPE #1. With less than 0.1 mg difference in weight, it clearly shows a reduction in T_m , and a decrease in peak area (see Table XXXII) representative of decreased ΔH_f , resulting from radiation exposure for crosslinking. These scan characteristics are indicative of fewer, smaller, less perfect crystals.

The dependence of T_m on the sample heating rate is not simple and is strongly affected by thermal history. Polymer crystallization involves the

Figure 30: Comparative DSC scan of LDPE #1 uncrosslinked (solid line) vs. 80 Mrad electron beam irradiated (broken line).

formation of an ordered state from a disordered state. This process may be induced to take different routes which lead to correspondingly different final states depending on the samples temperature state, cooling rate or annealing history. However, melting may be considered an opposite process of crystallization since its end state is the common disorder of the melt. On the surface, crystallization may seem irrelevant, but the melt process often provides information on the nature of the crystalline structure being destroyed. Therefore, the effects observed during melting are dependent on both the previous crystallization history of the sample and the conditions under which the melting took place (36). For those reasons, with the exception of a few samples intended for comparisons, all samples were heat treated with identical heat/cool/heat cycles. The first heat cycle was intended to erase any previous thermal history; the cool cycle was to establish a consistent crystallization process; and the second heat cycle was intended for data collection.

Table XXIX lists the data collected from the preliminary tests on HDPE #1 to determine whether the change in T_m and ΔH_f would be significant at these dose levels to warrant further testing. As can be seen by Figures 31 and 32 which graphically display the results, the changes are indeed not only significant, but also consistent. As the radiation dose increased, T_m and ΔH_f decreased. The melt temperature decreased by 7% compared to a 25% reduction in ΔH_f .

Table XXIX: T_m and ΔH_f data from HDPE #1 electron beam crosslinked at varied dose levels.

Dose	Second Heat	
	$T_m(^{\circ}\text{C})$	$\Delta H_f(\text{J/gm})$
0	134.0	217.8
5	133.2	204.6
10	131.4	195.6
20	130.0	184.0
40	127.6	177.0
80	124.7	163.8

Figure 31: DSC second heat T_m values after irradiation of HDPE #1 at varied dose levels

Figure 32: DSC second heat ΔH_f values after irradiation of HDPE #1 at varied dose levels

Also apparent in this data is a decrease in the rate of change of T_m and ΔH_f with increased dose. To determine the limiting rate of change and/or the leveling off point would require further testing at higher doses. However, the data reported here does imply that the majority of the 25% change in ΔH_f after 1000 Mrads observed by Luo et al. (14) occurred within the first 100 Mrads exposure.

To assure reproducibility of data, five samples of HDPE #1 were tested in duplicate with excellent results. The five samples tested included the uncrosslinked control and one each representing all four crosslinking procedures at maximum dose. In the worst case, the range of values encompassed 1.1% for ΔH_f and 0.6% for T_m . Each test requires approximately one and one half hours per sample to complete. Therefore, all remaining samples were tested once.

Tables XXX, XXXI and XXXII list the data acquired for T_c , T_m and ΔH_f respectively for all sets of blends at maximum dose by each of the four

Table XXX: DSC crystallization temperature data comparing all blends at 80 Mrads dose of each crosslinking method to the uncrosslinked control.

Sample	e Beam T_c (°C)	Co(N ₂) T_c (°C)	Co(air) T_c (°C)	Chemical T_c (°C)	Control T_c (°C)
HDPE #1	106.8	104.7	105.9	107.4	112.7
LDPE #1	95.3	93.5	95.0	98.0	102.7
HDPE #1/EVA	107.1	105.9	105.4	105.3	112.5
HDPE #1/EEA	105.8	103.6	104.5	105.1	111.9
LDPE #1/EVA	95.4	93.6	98.5	96.0	102.5
LDPE #1/EEA	93.5	92.7	98.1	95.0	102.8
EVA	60.2	60.4	61.3	55.5	63.4
EEA	70.4	71.8	76.3	71.8	77.7
HDPE #2	110.7	108.9	109.3		116.5
LDPE #2	88.0	86.7	93.8		95.9

Table XXXI: DSC melt temperature data comparing comparing all blends at 80 Mrads dose of each crosslinking method to the uncrosslinked control.

Sample	e Beam T _m (°C)	Co(N ₂) T _m (°C)	Co(air) T _m (°C)	Chemical T _m (°C)	Control T _m (°C)
HDPE #1	124.7	123.4	124.7	122.9	134.0
LDPE #1	110.4	110.2	111.0	113.0	117.5
HDPE #1/EVA	124.7	122.1	125.8	120.5	133.1
HDPE #1/EEA	121.2	119.0	123.7	121.0	130.1
LDPE #1/EVA	109.1	108.1	109.7	111.7	116.6
LDPE #1/EEA	108.4	108.0	113.3	110.2	115.9
EVA	78.6	78.3	80.5	77.6	85.8
EEA	90.1	90.1	94.1	92.1	98.5
HDPE #2	125.0	123.6	125.2		135.4
LDPE #2	102.1	101.9	102.8		111.0

Table XXXII: DSC heat of fusion data comparing all blends at 80 Mrads dose of each crosslinking method to the uncrosslinked control.

Sample	e Beam (J/gm)	Co(N ₂) (J/gm)	Co(air) (J/gm)	Chemical (J/gm)	Control (J/gm)
HDPE #1	163.8	154.0	163.0	139.5	217.8
LDPE #1	122.3	106.0	123.3	111.5	129.9
HDPE #1/EVA	110.6	103.5	113.4	77.1	134.3
HDPE #1/EEA	97.9	87.6	104.3	88.7	122.5
LDPE #1/EVA	73.2	72.1	83.4	70.6	84.5
LDPE #1/EEA	82.1	80.0	90.6	80.2	94.0
EVA	34.1	34.1	37.6	32.9	39.8
EEA	39.3	40.0	44.6	41.6	46.3
HDPE #2	156.5	157.3	161.2		215.7
LDPE #2	92.6	87.8	100.3		102.5

Figure 33: DSC crystallization temperature data comparing all blends of each crosslinking method after 80 Mrads dose.

Figure 34: DSC melt temperature data comparing all blends of each crosslinking method after 80 Mrads dose.

Figure 35: DSC heat of fusion data comparing all blends of each crosslinking method after 80 Mrads dose.

Figure 36: DSC crystallization temperature data comparing all blends of each crosslinking method after 80 Mrads dose.

Figure 37: DSC melt temperature data comparing all blends of each crosslinking method after 80 Mrads dose.

Figure 38: DSC heat of fusion data comparing all blends of each crosslinking method after 80 Mrads dose.

crosslinking techniques as well as the control. This data is consistent with previous observations. All formulations show a substantial decrease in the T_m and ΔH_f after crosslinking.

A somewhat more subtle observation is that the change in T_m and ΔH_f is not as large for LDPE formulations and for copolymers as it is for HDPE formulations. A likely explanation for this is that the degree of branching in the low density polyethylenes is such that the number of branches greatly exceeds the number of crosslinks even for relatively high crosslink densities. Therefore, the effect on depression of T_m and ΔH_f caused by crosslinking is not as significant because of the depression already caused by the more highly populated branches.

Figure 39: T_c plot of LDPE #1 after 80 Mrads (solid line) and 10 Mrads (broken line) by ^{60}Co in air.

Figures 33 through 35 graphically display the data from the preceding tables. Because the data is somewhat compact, Figures 36, 37, and 38 were made by excluding the last four formulations. From these graphs, we see that the data points are not only quite closely bunched together, but also there is frequent crossover and intermingling. The DSC is unable to provide a means which enables us to consistently identify one crosslinking method from the others

Although this procedure provides data that is inconclusive in allowing one to unconditionally distinguish between crosslinking methods, two interesting observations were made which could be of assistance when coupled with other information. The first was that eight of the ten formulations displayed doublet crystallization peaks when irradiated with ^{60}Co in air. The doublet becomes less obvious with decreased dose and undetectable below a 20 Mrad dose. Figure 39 shows the distinct difference in the cooling cycle for LDPE #1 when irradiated at 10 Mrads vs. 80 Mrads by ^{60}Co in air. This doublet was not observed in any of the ten formulations when crosslinked by the three other methods.

Table XXXIII: Comparing first and second heat values of T_m and ΔH_f for HDPE #1 with different crosslinking methods.

Method of X-Linking	Beam Dose (Mrad)	First Heat		Second Heat	
		T_{m1} ($^{\circ}\text{C}$)	(J/gm)	T_{m2} ($^{\circ}\text{C}$)	(J/gm)
None	0	131.8	198.7	134.0	217.8
Electron Beam	80	130.3	189.8	124.7	163.8
^{60}Co in N_2	80	130.7	192.2	122.7	154.5
^{60}Co in air	80	131.5	195.9	124.1	164.7
Chemical		122.4	124.1	123.1	138.9
Electron Beam (After Heated Above T_m)	80	128.8	162.0	124.9	165.5

The second observation became apparent from Table XXXIII when comparing T_m and ΔH_f from the first and second heat cycles of the DSC experiment. For the first heat cycle, the values for T_m and ΔH_f show only subtle differences between the control and the radiation crosslinked polymers. It is not until the second heat cycle that the drop in these values occur. But, if the radiation crosslinked sample has already been exposed to a temperature in excess of its melting point, the T_m and ΔH_f depression between the first and second heat cycles will not be observed. As for the chemically crosslinked samples, the T_m and ΔH_f values are already depressed because they were cured above their melting point.

Chemical crosslinking of polyethylene is done while molten, thus inducing a high crosslink density. As a result, the molecules have difficulty rearranging to form crystals. In contrast, when samples are crosslinked by irradiation at ambient temperature, there is no drop in the crystalline melting point. But once heated above the melt, their previously existing crystal structure is disturbed and when cooled will never return to the same level of crystallinity due to the restrained movement imposed by the crosslinks.

Testing by DSC does not provide a means of distinguishing between the four methods of crosslinking. It does, however, provide clues which could conditionally assist one in making some limited conclusions about the method of crosslinking. First, if the crystallization peak is a doublet, there is a strong possibility the sample has been irradiated by greater than 20 Mrads with ^{60}Co in air. Second, if there is a substantial drop in T_m and ΔH_f between the first and second heat cycles, the sample has probably been radiated at ambient temperature rather than chemically cured above the melt.

APPLICATION ON UNKNOWNNS

To test the capabilities of the results from this study, four crosslinked unknown samples were requested by the author. These four samples were to consist of polyethylene or polyethylene/ copolymer blends representing any or all of the four crosslinking methods studied. The samples were received and marked A through D. Their general appearance was recorded as:

Sample A 20 mil thick gray-black flexible film

Sample B 125 mil thick hard, rigid black slab

Sample C 25 mil thick black flexible film

Sample D 20 mil thick clear, transparent film.

Analysis of all samples by a thermogravimetric analyzer (TGA) was necessary prior to conducting tests for crosslinking. Since at least three of the four samples appeared to contain a substantial quantity of fillers or other additives, TGA would be necessary for determining the "true" polymer weight for the percent gel values as a percent of the polymer only. In addition, it would be an important test in determining whether the level of carbon black was too high for conducting transmission spectroscopy on films.

Samples A, B, and C contained between 5 and 25% carbon black. Other additives were present ranging from 8 to 30%. Only sample D appeared to be a pure polymer system. Therefore, the percent polymer for each sample was recorded in Table XXXIV for percent gel calculation. Spectral data could be acquired on Sample D as a pure polymer, but xylene extracts were necessary for samples A, B, and C.

Because of the presence of the other additives, a solvent separation method was used to purify the polymer. After extraction with refluxing xylene, the solvent was allowed to evaporate to near dryness. A 1:1 mixture of methanol and chloroform was added and thoroughly mixed at room temperature. The dissolved polymer became an insoluble, flocculent mass making possible thorough rinsing by the solvent blend. The sample was then

centrifuged. The inorganic fillers and halogenated organics precipitated, the soluble additives such as plasticizers remained in solution and the polymer formed a caked mass at the top. This purification process was repeated three times before the xylene extracted polymer was cast onto a salt plate for acquiring spectral data. All other tests were conducted as previously discussed in the experimental section of this report.

Table XXXIV lists the data for these tests and the conclusions based on the results. Sample A, with a trans-vinylene S_r greater than 0.75 appears to be irradiated. The S_r for carbonyl was badly masked by an additive which could not be removed and therefore was not available. Sample B, had a 12% decrease in ΔH_f and showed no evidence of a doublet T_c by DSC. It fell below the linear boundary separating the chemically crosslinked from the irradiated polymers. In addition, it had high S_r for the ketone carbonyl band. Considering all factors, it an excellent candidate for irradiation by ^{60}Co in air at less than 20 Mrads. Sample C had low S_r for trans-vinylene and fell above the boundary indicative of being chemically crosslinked. Sample D had similar properties as B. It too was concluded to be irradiated by ^{60}Co in air.

Although there was some question as to Samples B and D because they did not fall in the cluster due to their low S_r for trans-vinylene, all four conclusions were correct. Sample A was electron beam crosslinked, Sample B was irradiated by ^{60}Co in air, Sample C was chemically crosslinked, and Sample D was not only irradiated by ^{60}Co in air, but was the dosimeter attached to sample B during the irradiation process. These results for samples B and D further confirm my suspicion that at lower levels of irradiation the cluster for ^{60}Co in air will expand making the distinction of this method less clear.

Table XXXIV: Test results and conclusions for unknown samples

Tests		Unknowns			
		Sample A	Sample B	Sample C	Sample D
I	TGA - % Polymer	57.19	83.69	69.75	100
II	Gel (% of Polymer)	73.99	76.48	88.61	45.19
III	DSC				
	T_{m2} (°C)	122.3	99.6	110.8	107.6
	$T_{m1} - T_{m2}$ (°C)	1.3	-1.5	1	0.1
	$H_{f1} - H_{f2}$ (J/gm)	3.9	-10.8	5.3	-8.3
	Doublet T_c	None	None	None	None
IV	IR Spectroscopy	extract	extract	extract	neat film
	S_r (trans-vinylene)	4.63	0.72	0.3	0.44
	S_r (carbonyl)		12.04		9.66
	$100S_r/\%$ Gel		15.74		21.38
	Boundary equation $y = 100(S_r) + 25$	NA	97 % gel < y	55.4 % gel > y	69.2 % gel < y
V	Conclusion - type of crosslinking	Irrad.	^{60}Co in Air	Chemical	^{60}Co in Air

CONCLUSIONS

As mentioned in the introduction, the main purpose of this study is to develop a method for distinguishing between four of the most common methods of polymer crosslinking. These methods are irradiation by electron beam, ^{60}Co in air, ^{60}Co in nitrogen, and by chemical curing. The first goal which has already been at least partially accomplished is to be able to distinguish between methods of crosslinking used in transparent, unfilled polymer systems. The final purpose is to successfully apply that method to complex polymer formulations by examining the xylene extracts for similar relationships. That, too has shown some degree of success based upon our results with the four unknown samples.

A quick summary of the test results from this study are:

1. For a specific level of radiation exposure, the crosslinking efficiency decreased relative to the polymer free radical's ability to react with oxygen. With every polymer or polymer blend tested, ^{60}Co in N_2 was the most efficient and ^{60}Co in air the least. This observed difference was most evident at doses above 20 Mrads, but the least evident at low doses less than 20 Mrads in HDPE.
2. The S_r for trans-vinylene absorption was distinctly lower for all chemically crosslinked polymers or blends tested. No further distinctions could be made. S_r values were consistent for all blends of all three irradiation techniques.
3. The S_r for ketone carbonyl absorption was distinctly lower for chemically crosslinked polymers and higher for all irradiated by ^{60}Co in air.
4. Two dimensional plotting of data points representing all samples and all crosslinking methods involving the above three characteristics displayed a distinctly separated, compact cluster representing chemically crosslinked polymers. A broader, less distinct cluster existed for polymers irradiated by ^{60}Co in air.

5. Two dimensional plotting of data points representing all polymers and methods of crosslinking making use of only the first two characteristics again displayed a distinct separation between chemically crosslinked and irradiation crosslinked polymers. This lead to the visual selection of an arbitrary boundary representing a linear discriminate by the equation:

$$\% \text{ Gel} = 100(S_r) + 25$$

In other words whenever the percent gel is in excess of 100 times the S_r of the trans-vinylene band plus 25, the sample is chemically crosslinked.

A less distinct, but evident, cluster of data points representing irradiation by ^{60}Co in air existed.

6. DSC scans showed a substantial decrease in T_m and/or ΔH_f values between the first and second heat cycles for all polymers irradiated at ambient temperature, provided they had never been exposed to heat above their melt temperature.
7. Only samples irradiated by ^{60}Co in air displayed a doublet T_c curve above 20 Mrads exposure.
8. Similar class separations between chemically crosslinked and irradiated polymers can be made with xylene extractions. The ketone carbonyl S_r values are inconsistent and sometimes immeasurable, making the distinction of ^{60}Co irradiation in air more difficult .

From the data presented in this study, we are able to clearly isolate and identify chemically crosslinked polymers. Although there are some definite characteristics aiding in the identification of polymers irradiated by ^{60}Co in air, the distinction is more ambiguous. No differences were observed for class separation of electron beam irradiated polymers from those irradiated by ^{60}Co in nitrogen.

There are several immediate extensions of this work. First, there is need for further clarification of class boundaries. Experimental data from additional

peroxides at varied blend ratios is needed. In addition, more data points are needed not only of the same polymers at lower dose levels, but also of the same class of polymers from different origins. This is especially important for materials irradiated by ^{60}Co in air. The additional data will aid in determining whether a true distinction from the other irradiation methods exists.

Second, from the preliminary tests conducted by CP-MAS, there is evidence that the changes in the crystalline and amorphous domains caused by the different crosslinking methods could be monitored. In addition to needing a variety of samples representing different polymers, different crosslinking methods and different degrees of crosslinking, NMR monitoring would require a comprehensive study involving careful temperature control, varied pulse delays, and experimentation in deconvolution for peak area measurement.

Finally, this study could easily become a candidate for multivariate analysis. There are many other tests that could provide additional data to the existing data from this study. In this study, only three major features were graphically displayed, one of which is the S_r for measurement of the trans-vinylene band. Additional data features which could be included are: bromine or iodine titration which determines all unsaturation, specific gravity tests, NMR data from the above proposed study, and incorporation of DSC data already studied in this report.

In conclusion, It has been observed that a method for identifying the type of crosslinking used in polymer processing could be a valuable tool in predicting the performance and potential usability of polymeric materials. It is hoped that the findings from this study will be useful in performing that function.

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Appendix

OBEY program for beam dose calculation on
Perkin-Elmer 7700 data station

```
do sclear
do display off
gclear
set wait off
do display on
&l5 *
do sclear
* This is an obey program for scanning the Polyethylene dosimeter,
* calculate its Spectroscopic Ratio (SR) and the beamdose (Mr.)
*
* Place the dosimeter sample on the holder and insert the holder
* into the sample holder.
*
* Check for the following conditions:
*     Baseline at ~ 90%T (need to check for the first sample only.)
*     slit program = narrow
*     scan time = 12 mins
*     place a shield in front of the sample
*
* When you are ready to begin, press the ENTER key.
do pause
do display off
inst chart off
do display on
* Press the ENTER key, enter your sample I.D. and press the ENTER key
do pause
do display off
&enter a!
do display on
do sclear
do display off
gclear
do display on
* Remove the shield.
```

```

do pause
scan x 2200 1900 1
view x
* PLACE A SHIELD IN FRONT OF THE SAMPLE.
do pause
do sclear
*
*
*
* MOVE THE CURSOR TO THE PEAK MIN. AND PRESS 'H'.
do display off
&cursor v1
do display on
do sclear
*
*
*
* MOVE THE CURSOR TO PEAK MAX. AND PRESS 'H'.
do display off
&cursor v2
calc v4 = aval(absr(x(v2)) - absr(x(v1)))
do display on
do sclear
do display off
gclear
do display on
* Remove the shield.
do pause
scan y 1020 920 1
view y
* PLACE A SHIELD IN FRONT OF THE SAMPLE.
do pause
do sclear
*
*
*
* MOVE THE CURSOR TO PEAK MIN. AND PRESS 'H'.
do display off
&cursor v5
do display on
do sclear
*

```

```

*
*
* MOVE THE CURSOR TO PEAK MAX. AND PRESS 'H'.
do display off
&cursor v5
calc v8 = aval(absr(y(v6)) - absr(y(v5)))
calc v9 = v8/v4
&if v9 < 0.9 then 115
&goto 120
&115 *
calc v10 = 6.13 * v9^2 + 24.15 * v9 - 2.59
&goto 125
&120 *
calc v10 = 7.05 * v9^2 + 25.29 * v9 - 2.59
&125 *
gcLEAR
do display on
do scLEAR
* The Spectroscopic Ratio is:  &v9
*
* The beam dose is:  &v10
do pause 30
do display off
vsave open append w4:dose
vsave w4:dose a1, v9, v10
vsave close w4:dose
output clear a2
do display on
&130 * Do you want to run another sample?
* Press the ENTER key first, then type "y" for "yes", type "n" for "no"
* and press the ENTER key again.
do pause
do display off
&enter a2
do display on
&if a2 = "y" then 15
&if a2 = "n" then 140
&error 135

```

```
&135 *
do sclear
&goto 130
&140 *
do sclear
do display off
gclear
do display on
*
* Reset the wavenumber to 4000 and reset the pen to 90% T on the I.R.
*
do pause
do sclear
*
* >>>>>>>>>This is The End of the Beamdose Program! <<<<<<<<<
*
*
do display off
set wait on
do display on
```