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POLYMER INDUSTRY

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September 1978

Presented at the
Second International Meeting on Radiation Processing,
Radiation's Current Success and Bright Future,
Miami, Florida
October 22-26, 1978

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ABSTRACT

A series of ethylene-carbon monoxide copolymers have been prepared by chemical catalysis and Co-60 gamma radiation induction, ranging in carbon monoxide content from 41 to 49%. A correlation has been established between the method of preparation, the carbon monoxide content of the copolymers and the mechanical properties of the resulting products. Present evaluations indicate that copolymers containing ~ 50% carbon monoxide prepared by Co-60 gamma induction have significantly improved mechanical properties over copolymers prepared by conventional chemical, free-radical catalysis. Based on these results, it is suggested that further experimentation be conducted in radiation-induced copolymerization especially with the use of electron beam machines presently available to industry.

INTRODUCTION

The objective of this program is to investigate the synthesis and usefulness of polyketones and polysulfones as energy conserving polymers in the ethylene polymer industry. Research performed at Brookhaven National Laboratory in the 1960's on radiation-induced copolymerization of ethylene (Refs. 1, 2) indicated that a high degree of polymerization (DP) could be obtained by the copolymerization of CO and of SO₂ with ethylene. The white solid polymers formed were identified as ethylene polyketones and ethylene polysulfones. The kinetics of the polyketone reactions indicated several significant differences between the lower temperature free-radical radiation induced reaction and the higher temperature thermocatalytic reaction. The literature data indicated lower molecular weight, waxy-type copolymers forming with peroxide-type catalysts at temperatures in the order of 130°C while high molecular weight, partially crystalline polymers of ethylene and CO, could be formed at 20° to 50°C. The copolymerizations were conducted at elevated pressure in the order of 500 to 1000 atm. Thus, there appeared to be the possibility of a unique feature of Co-60 gamma radiation for inducing high DP polyketones and polysulfones at low temperatures.

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Besides the unique possibilities of radiation polymerization, the incentive to substitute low cost materials such as CO and SO₂ for the more expensive ethylene in producing a bulk polymer in the large ethylene polymer industry market seemed exciting. In the pre-oil embargo days, the cost of ethylene was as low as 2¢/lb. Recently ethylene cost has been as high as 18¢/lb and since it is made from natural gas or from oil there has been some concern for allocation of adequate supplies of feedstock. The incentive for substituting or incorporating CO and SO₂ in the ethylene polymer market and in producing an energy conserving polymer is quite high today. Furthermore, CO can be made from the large indigenous US coal supplies and SO₂ may actually become a large scale waste product from the desulfurization of coal for the power and metallurgical industries. It has been estimated (Ref. 3) that penetrating only 25% of the bulk ethylene polymer market with low cost CO would conserve about 100 billion cu ft/yr of natural gas or about 0.1 quad/yr energy equivalent and the savings in cost would amount to over \$280 million annually.

Recognizing these incentives, (as a licensor of a CO recovery system) the Tenneco Corporation proposed to enter into a joint program with Brookhaven National Laboratory and sponsorship of the Department of Energy (DOE) to investigate polyketones and polysulfones as an energy and materials conserving program for the Division of Industrial Conservation of DOE.

It has also been indicated (Ref. 3) that if a radiation induced process is uniquely required for the copolymerization process, that it would be technically and economically more attractive to use electron beam radiation in place of Co-60 gamma isotopic radiation. To our knowledge there has been no work performed in this copolymer system using electron beam radiation.

The scope of the first phase of this program is to accomplish the following tasks:

1. Produce quantities of ethylene-CO copolymers and ethylene-SO₂ copolymers with the use of Co-60 gamma radiation of several different compositions for evaluation and characteristics of properties. The polymer characteristics are to be compared to polymers produced by thermal catalytic means. The latter experiments are to be conducted at locations other than at Brookhaven. The radiation experiments are to be conducted at BNL and the characterization of the product is to be performed by Tenneco.
2. Produce quantities of ethylene-CO copolymers and ethylene-SO₂ copolymers with the use of electron beam radiation. Since no work has been done in this direction in the past, basic design of a suitable high pressure gas vessel experiment in conjunction with an electron beam machine must be conducted. One of the main differences between a high energy electron machine radiation and Co-60 is the several orders of magnitude increase in dose rate of the electron machine over the Co-60 radiation. Because of this high dose rate, it may be possible to trade-off lower pressures for higher intensities. The characteristics of the product will be determined by Tenneco and the radiation will be conducted by Brookhaven National Laboratory (BNL) both with the electron machine located at BNL and possibly at the site of an industrial electron machine manufacturer on Long Island.
3. Preliminary design and a cost estimate of an electron machine radiation pilot plant will be initiated.

It is the purpose of the first phase of the program to establish the desirability of using electron machine radiation for producing Et-CO and Et-SO₂ copolymers. The potential value of the product polymer in the bulk ethylene polymer market is also to be established both from a processing and marketing point of view.

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In this report, work on Task 1, the Co-60 gamma radiation induced polymerization, the thermocatalytic induced polymerization, and the characterization of the copolymers from each of the experiments are presented and evaluated.

DESCRIPTION OF Co-60 GAMMA RADIATION EXPERIMENTS

The procedure for the Co-60 gamma induced radiation experiments was based largely on the previous work at BNL (Refs. 1,2). The copolymerizations were carried out in a 100 cm³ high pressure Inconel vessel measuring 1" I. D. by approximately 11" long and provided with a rupture disc assembly and valve as shown in Figure 1. A pressure gauge was mounted approximately fourteen feet above the top of the vessel to permit observation of the system pressure during submergence of the vessel in the Co-60 gamma pool (see Figure 2). A tee with a valve was provided for filling and venting the assembled apparatus. The reaction vessel was placed in a holder with tapered legs that facilitated alignment and positioning of the assembly in the annular opening of the Co-60 source holder at the bottom of the gamma pool. The long 1/4" gauge line was supported by an extension of one of the reaction vessel holder legs that also served as a handle and support rod for the assembled apparatus during filling and handling before and after irradiation. The Co-60 gamma pool type facility at Brookhaven was used for conducting the irradiation polymerization. Since no air duct was used with the Co-60 source, the apparatus was in contact with the gamma pool water which measured 10-13°C in the region of the source. No internal reaction vessel temperatures were taken.

The polyketones were prepared by charging the evacuated apparatus with ethylene and CO premixed in gas cylinders (C. P. grade supplied by Matheson Gas Products) and pressurized by means of a stainless steel diaphragm compressor. The fill connection was disconnected and the reaction apparatus was then transferred to the gamma pool for equilibrating with the pool water temperature prior to insertion into the Co-60 source holder annulus for irradiation. Since there is a reduction in volume during polymerization and no attempt was made to replenish loss of reactants by means of a compressor, all of these runs were of the falling-pressure type. The radiation energy inside the reaction vessel was measured by using a Fricke dosimeter. After each run, excess gas was vented and the polymer, in the form of a solid white mass, was recovered and weighed for determination of yield.

The polysulfones were prepared in a similar manner except that a different filling procedure was required, since the SO₂ component forms a liquid phase at the experimental pressures. The SO₂ was transferred batch-wise as a gas at low pressure and then condensed into the chilled reaction vessel. From the known pressure, volume, and temperature of the transfer system, the quantity of SO₂ collected in the reaction system was calculated. The vessel containing this known quantity of SO₂ was then charged with pure ethylene gas to the desired pressure by means of the compressor. No attempt was made to segregate product made in the liquid phase from product made in the gas phase by use of screens, as had been done in the previous work (Ref. 1).

SYNTHESIS OF POLYKETONES USING CHEMICAL FREE RADICAL CATALYSIS

The standard procedure used to prepare the ethylene-carbon monoxide copolymers was a modification of the Brubaker et al. (Ref. 4) batch technique. A two liter thoroughly cleaned stirred reactor, capable of withstanding pressures of 25,000 psig at 300°C (600°F), was prepurified by removing all air by a nitrogen purge. The selected gas mixtures of ethylene and carbon monoxide were premixed in an intensifier, and then as the reactor was vented to remove the nitrogen, the intensifier was precompressed to a pressure greater than the reactor pressure,

and the intensifier charge transferred to the reactor. The desired catalyst dissolved in solvent (heptane) is volumetrically pumped into the process line at the top of the reactor. This is followed by an injection of the compressed gas feed to clear the common process line of catalyst and to make a final pressure adjustment. As the reaction progresses, repeated catalyst comonomer feed (i.e., to maintain the reaction pressure constant, by replacing the reacted comonomer gas mix) injections are made to prolong the polymerization to increase polymer yield. In order to give a low order exotherm during the polymerization, the catalyst solution is injected every half-hour. The reaction is continued several hours after the final catalyst injection. The heat is then turned off automatically and the reactor and contents allowed to cool overnight. Unreacted monomer is vented, the reactor opened, the product recovered and worked up.

Fig. 1. High pressure vessel with valve and rupture disc assembly (internal volume 110 cm³) used for Co-60 gamma irradiation of ethylene and CO and ethylene SO₂.

Fig. 2. High pressure vessel with remote pressure gauge and support for inserting into Co-60 gamma facility.

Co-60 GAMMA RADIATION EXPERIMENTAL RESULTS

The experimental results for the copolymerization of ethylene and CO by Co-60 gamma induced radiation are given in Table 1. Initial reaction pressures ranged between 347 and 619 atm (5100 and 9150 psi) and final pressures were between 245 and 578 atm (3600 and 8500 psi). Highest overall polymerization rates were obtained with the 48.8% CO - 51.2% ethylene mixture (22.2 to 34.2 g/l-hr at G values of 2100 to 3970 molecules/100 eV), and the lowest rates were obtained with the 89.6% CO - 10.4% ethylene mixture (0.30 and 0.45 g/l-hr at G values of 31 and 46 molecules/100 eV). Relatively good rates were obtained with the 9.4% CO - 90.6% ethylene mixture (17.3 to 29.4 g/l-hr at G values of 1700 to 3120 molecules/100 eV). In general, these results are in agreement with the previous work at BNL,

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(Ref. 1) where the effects of composition, pressure, temperature, and radiation intensity were extensively investigated. The highest rates were obtained near the azeotropic composition of 48.5% CO - 51.2% ethylene. At this point the composition of the polymer formed is equal in concentration to the gas composition.

TABLE 1 Co-60 Gamma Radiation Copolymerization of Ethylene and CO
Experimental Results

Temperature: 10-13°C
Radiation Intensity: 7.11x10⁵ rads/hr

Total Reaction System Volume: 130 cm³
Volume in Radiation Field: 110 cm³

Run No.	Initial conc. % CO	Pressure, atm Initial Final	Initial wt., g	Time, hr	Product weight, g	Overall rate, g/l-hr	Overall G value, molecules/100 eV
1	9.4	592 442	65.0	1.50	2.85	17.3	1700
2	9.4	456 354	61.7	1.50	4.2	25.7	2720
3	9.4	524 340	63.3	2.00	6.3	28.6	2990
4	9.4	347 245	58.2	2.07	3.9	17.3	1940
5	9.4	565 327	64.3	3.00	9.7	29.4	3120
7	48.8	578 408	62.6	3.00	10.3	31.2	3420
9	48.8	595 340	63.6	5.00	18.8	34.2	3970
10	48.8	592 538	63.6	1.50	4.2	25.5	2610
12	89.6	602 578	62.2	22.33	1.1	0.25	46
14	89.6	619 470	62.2	22.62	0.75	0.30	31
15	48.8	599 388	63.6	4.50	13.2	26.7	2110
16	48.8	599 395	63.6	4.58	11.2	22.2	2410

G-Value Calculations:

$$G = \frac{9.65 \times 10^{11} P}{M.W. \times D \times V}$$

P = Weight of product polymer, gms

D = Total dose in rads = (I)(t)

M. W. = mol. wt. of unit polymer (For Et-CO
M.W. always equals 28; For Et-SO₂
depends on composition)

I = Radiation intensity, rads/hr

The experimental results for copolymerization of ethylene and SO₂ by Co-60 gamma induced radiation for runs 11 and 13 are given in Table 2. Since the reaction times were the same (0.333 hr) and the initial pressures were essentially the same (537 and 544 atm for runs 11 and 13, respectively), the increased amount of product in run 13, respectively, the increased amount of product in run 13 (42.1 vs 32.1 g) can be attributed to the doubled quantity of SO₂ in run 13 (51.0 vs 25.5 g), which was present mainly in the liquid phase. The overall rates (875 and 1148 g/l-hr for runs 11 and 13, respectively) and G values (5.58×10^4 and 6.23×10^4 molecules/100 eV for runs 11 and 13, respectively), are based on the total volume in the radiation field (110 cm³) and thus are average values for the gas and liquid phase reactions. More quantitative data are available in the work done previously at BNL (Ref. 2). It is noted that the rates and G values for the polysulfone formation are more than an order of magnitude higher than polyketone formation.

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TABLE 2 Co-60 Gamma Copolymerization of Ethylene and SO₂
Experimental Results

Temperature: 10-13°C		Radiation Intensity: 7.11×10^5 , rads/hr		Total Reaction System Volume: 130 cm ³		Volume in Radiation Field: 110 cm ³	
Run No.	Initial Charge SO ₂ , g	Pressure, atm Initial Final	Initial Tot. wt., g	Time, hr	Product weight, g	Overall rate, g/l-hr	Overall G value, molecules/100 eV
11	25.5	537 238	81.3	0.333	32.1	875	5.58×10^4
13	51.0	544 218	97.7	0.333	42.1	1148	6.23×10^4

Product Polymer Composition: 65 wt% SO₂
35 wt% Et
Unit M.W. = 43.2

EXPERIMENTAL RESULTS FROM CHEMICAL FREE RADICAL COPOLYMERIZATION OF ETHYLENE-CARBON MONOXIDE

Details of the results obtained from the copolymerization of ethylene-carbon monoxide by chemical-free-radical catalysis are summarized in Tables 3 and 4.

TABLE 3 Ethylene-Carbon Monoxide Copolymers Polymerization Charge and Process Conditions

Sample No.	Ethylene (Vol/P)	CO (Vol/P)	Catalyst	Solvent	Pressure (psig)	Temp. (°C)	Time (hr)	gm. Yield (crude)
E-099-31	70%	30%	0.29G Vazo 52	14.7 ml Heptane	10,000 (constant)	70	5.6	26
E-099-34	70%	30%	0.89G Lauroyl Peroxide	65.0 ml Heptane	15,000 (constant)	80	5.7	46.3
E-099-36	60%	40%	0.22G Vazo 52	32.5 ml Heptane	15,000 (constant)	70	8.5	200.2
E-099-52BR	90.6%	9.4%	Co ⁶⁰ 7.11×10^5 rads/hr.	-	8,700 (falling)	12	1.5	2.85
E-099-53BR	90.6%	9.4%	Co ⁶⁰ 7.11×10^5 rads/hr.	-	6,700 (falling)	13	1.5	4.24
E-099-54BR	90.6%	9.4%	Co ⁶⁰ 7.11×10^5 rads/hr.	-	7,700 (falling)	11.5	2.	6.28
E-099-70BR	51.2%	48.8%	Co ⁶⁰ 7.11×10^5 rads/hr.	-	8,500 (falling)	9.5	3.	10.3
E-099-71BR	51.2%	48.8%	Co ⁶⁰ 7.11×10^5	-	8,750 (falling)	10	3.	18.8
E-099-76BR	51.2%	48.8%	Co ⁶⁰	-	8,700	9.5	1.5	4.2

TABLE 4 Ethylene-Carbon Monoxide Copolymers Analytical and Polymer Characterization

Sample No.	XC	XH	XO	$\bar{X}$ C ₂ H ₄	$\bar{X}$ CO	T _M (Min. °C)	T _M (Max. °C)	$\bar{X}$ Crystallinity	Modulus (psi)	Strength (psi)	Elongation %
E-099-31	67.8	8.2	23.9	58.2	41.8	141	165	21.7	17,300	2,035	27
E-099-34	66.9	8.1	25.0	56.2	43.8	160	173	30.1	54,700	2,510	5.6
E-099-36*	66.0	7.9	26.1	54.4	45.6	165	190	28.7	-	-	-
E-099-52BR	68.3	8.3	23.4	59.1	40.9	140	160	31.1	48,609	2,082	7
E-099-53BR	67.5	8.3	24.2	57.6	42.3	134	156	30.9	57,593	2,528	7
E-099-54BR	67.6	8.3	24.1	57.6	42.3	129	156	29.4	49,710	2,759	15
E-099-70BR	64.6	7.3	28.1	50.8	49.2	215	222	38.5	66,545	4,364	9
E-099-71BR	65.3	7.6	27.1	52.6	47.4	212	227	47.8	84,390	3,008	6
E-099-76BR	64.5	7.4	28.1	50.8	49.2	221	230	47.6	87,640	5,920	19.5

* Thermally unstable, impossible to evaluate

Variables as pressure, ethylene/carbon monoxide ratio, temperature, and solvent have been shown by Brubaker et al. (Ref. 4) to profoundly affect the composition, molecular weight, and other polyketone properties. However, in this particular study, based on Brubaker's and Starkweather's (Ref. 5) data, a very narrow range of reaction conditions was selected. Since it is known that an increase in temperature lowers the CO content and molecular weight, all runs were at 70°C except for the lauroyl peroxide run at 80°C (sample #E-099-34). Because of insufficient data (i.e., only one run at 80°C) plus the inability to determine the molecular weight due to the insolubility of the $\geq 40\%$ carbon monoxide containing copolymers, the effect of the reaction temperature on these experiments cannot be determined. The ethylene-carbon monoxide ratio was kept at 70/30 except for one run (#E-099-36). Again, the data is insufficient for a definitive statement about the effects of an increased carbon monoxide in the comonomer mix.

The effect of progressively higher pressures at constant temperature (i.e., VAZO 52, 70°C) on conversion (i.e., an increase in pressure results in an increase in conversion in the copolymerization of ethylene and carbon monoxide) is noted in Table 3 for sample E-099-36 (excluding a possible increased CO concentration-effect in E-099-36). If this is a real observed effect, then it is in keeping with the observations of Brubaker et al. (Ref. 4).

CHARACTERIZATION AND EVALUATION OF THE EXPERIMENTAL ETHYLENE-CARBON MONOXIDE COPOLYMERS

Polymer characterization studies of the experimental ethylene-carbon monoxide copolymers were carried out in the Tenneco Chemical Inc. (TCI) laboratories. Due to the relative insolubility of ethylene-carbon monoxide copolymers, the molecular weights (i.e., by GPC) and NMR measurements could not be carried out on these products. As a result, only the solid state properties of the copolymers were evaluated (such as melting point, % crystallinity, tensile strength, tensile modulus, and % elongation). IR measurements were made on KBr pellets containing ground up, representative portions of the copolymer samples. The IR results were used for identifying the copolymers as polyketones, and the results were essentially the same as those found by Brubaker et al. (Ref. 4) and Steinberg et al. (Ref. 1).

Melting Points and Crystallinity

First-order transition temperatures were determined with a Perkin-Elmer differential scanning calorimeter (DSC), Model #2 at a scan speed of 20°C/minute. Temperature accuracy was assured by calibration with a series of melting point standards and the energy calibration was made with a sample of high purity indium. Table 4 collates the melting points, and percent crystallinity data of all the ethylene-carbon monoxide copolymers as a function of the percent carbon monoxide present in the copolymers, independent of the method of synthesis. Some of the copolymers were formed at temperatures above 20°C (except for the samples prepared at BNL), but were not subjected to thermal treatment before the DSC scan. The temperature at the onset of melting was determined from the point of deflection from the base line, and in agreement with Starkweather (Ref. 5) and Steinberg et al. (Ref. 1), the melting point was taken at the point at which the curve returns to the base line (i.e., the temperature at which the last vestige of crystallinity was lost). A peak maximum indicates the temperature and time at which the transition was proceeding at the maximum rate.

An examination of the data in Table 4, shows that as the amount of carbon monoxide in the copolymer increases, the melting point of the copolymer increases. There is general agreement (see Starkweather (Ref. 5) and Steinberg et al. (Ref. 1)) that this effect is related to the influence of the noncrystallizable CO-unit. It is felt that in the 40% carbon monoxide containing polymer, the varying ethylene chain length sequences interfere with the crystal structure of an alternating copolymer made-up of a six carbon repeat unit

Above 40% and approaching 50% carbon monoxide containing system, the melting point rapidly increases. This rapid increase in crystalline melting is probably due to an increase in the crystallizable $-\text{CH}_2-\text{CH}_2-\text{CO}-$ units (and a decrease in the non-crystallizable $-\text{CH}_2-\text{CH}_2-$ units). Using Flory's equation

$$\frac{1}{T_m} - \frac{1}{T_{m_0}} = - \frac{R}{\Delta H_f} \ln X$$

$$X = \frac{y}{1-y} = \text{fraction of crystallizable units}$$

$$y = \text{the concentration of } -\text{CH}_2\text{CH}_2-\text{CO}- \text{ units}$$

$$T_m = \text{absolute melting point}$$

$$R = \text{gas constant}$$

$$\Delta H_f = \text{heat of fusion}$$

Starkweather (Ref. 5) calculated the heat of fusion of the $-\text{CH}_2\text{CH}_2\text{CO}-$ units, and thereby the entropy of fusion for the same system. A comparison of this latter value (1.15 e.u./mol of chain atoms) with the value of the entropy of fusion of the polyethylene chain unit ($-\text{CH}_2\text{CH}_2-$), (2.29 e.u./mol of chain atoms) showed that the higher melting point of the ethylene-carbon monoxide copolymers is due to the lower entropy of fusion on the $-\text{CH}_2\text{CH}_2\text{CO}-$ unit vs the $-\text{CH}_2\text{CH}_2-$ unit, and

not to a higher heat of fusion of the former. The possible factors contributing to a lower entropy of fusion of the units in a 1:1 ethylene-carbon monoxide copolymers are (a) restricted rotational isomerism above the melting point, and (b) onset of motion and disorder below the melting point.

Note that the percent crystallinity was determined by first measuring the area under the DSC curve, thereby obtaining a value of ΔH_f of the copolymer, and comparing this value to the standard, completely crystalline polyethylene, $\Delta H_f = 66.3$ cal/g.

Mechanical Properties

The mechanical data (i.e., modulus, strength, and % elongation) shown in Tables 3, 4, and 5 were obtained using an Instron Tester. An analysis of these data indicates that perhaps two factors lead to improved mechanical properties; (a) equal amounts of carbon monoxide and ethylene produce better tensile modulus and tensile strength than polyethylene or low carbon monoxide copolymers, and (b) the products obtained by Co-60 radiation suggest that this method of preparation, at present, leads to materials with more desirable tensile properties. Even though the crystalline morphology of these experimental copolymers is not known, it seems reasonable to suggest that the observed mechanical differences between samples are intimately involved in chain structure and perhaps stereoregularity. The effect of molecular weight has to be considered as well. However, as noted above (i.e., the relative insolubility of high carbon monoxide containing copolymers), it is impossible to determine the relative molecular weights of the samples, and thereby the role of molecular weight on the mechanical properties on these copolymers is unknown.

It was noted specifically that an ethylene CO copolymer containing approximately 50% carbon monoxide (i.e., prepared by Co-60 induction) had substantially improved tensile properties (i.e. tensile modulus and tensile strength) as compared to an ethylene copolymer containing approximately 46% carbon monoxide prepared by chemical free radical catalysis (See Table 5). No difference in percent elongation (i.e. brittleness) was found for copolymers produced either by Co-60 or chemical free radical catalysis. It is not known at this time the structural reasons for the observed brittleness of these samples.

TABLE 5 General Properties of Ethylene-Co Copolymers

<u>Catalyst System</u>	<u>Melting Point Range, °C</u>	<u>Carbon Monoxide Content Range, %</u>	<u>Tensile Modulus, psi</u>	<u>Tensile Strength psi</u>	<u>% Elongation</u>
1. Chemical-Free-radical	165-190	42-46	17,000-55,000	2,000-2,500	7 ^a
2. Co ⁶⁰ Radiation (Free Radical; Brookhaven)	129-221	41-49	49,000-88,000	2,100-6,000	7-20 ^a
3. Low Density Polyethylene	120	-	6,300	3,000	1,000

^a All samples were brittle

CONCLUSIONS

A series of ethylene-carbon monoxide copolymers have been prepared by chemical and Co-60 gamma initiation, ranging in carbon monoxide content from 41 to 49%.

A correlation has been established between the method of preparation, the carbon monoxide content of the copolymers and the mechanical properties of the resulting products.

Present evaluations indicate that ~ 50% carbon monoxide copolymers prepared by Co-60 gamma induction have significantly improved mechanical properties over copolymers prepared by traditional chemical free-radical catalysis (which were found to contain $\leq$ 46% CO).

Based on these results, it is suggested that further experimentation be conducted in radiation-induced copolymerization. Based on equipment now presently available to industry, the study of radiation induction should center around electron beam catalyzed reactions.

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** This work has been performed under the auspices of the U. S. Department of Energy under Contract No. EY-76-C-02-0016.