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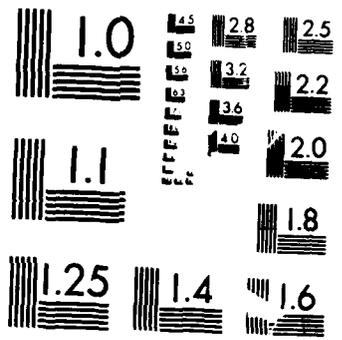
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**CHARACTERIZATION AND SELECTION
OF POLYMER MATERIALS FOR
BINARY MUNITIONS STORAGE -
PART 3: BRANCH CONTENT DETERMINATION**

AD-A187 418

C. RICHARD DESPER
MATERIALS CHARACTERIZATION DIVISION

September 1987

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ABSTRACT

Previous studies of potential failure mechanisms in polyolefin containers for binary munitions have established that good environmental stress cracking resistance (ESCR) is an essential property of a successful candidate resin. In this regard, it was also found that the linear low density polyethylenes (LLDPE's) offered performance advantages, and that the key resin characteristic influencing ESCR is the extent of short-chain branching. A characterization method which involves using precision lattice parameter determination for correlation with the branch content has been implemented. The data acquisition method obtains the required wide angle X-ray scattering (WAXS) data at greatly enhanced speed, without sacrificing any accuracy. The data acquisition system combines a position-sensitive X-ray detector with a 65 kilobyte microcomputer capable of operating as a multichannel analyzer and of performing immediate data analysis. The method is applied to the determination of branch content in a series of polyethylene resins for binary munitions storage. In addition, the resins are characterized and compared in terms of crystallinity and molecular weight distribution.

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INTRODUCTION

Review: Characterization of Short-Chain Branch Content

This laboratory has had a continuing project^{1,2} for determining the materials properties required for storage of DF (methylphosphonic difluoride) over extended periods of time and at elevated temperatures. The materials having the best combination of the requisite chemical resistance and long-term stability are polyolefins; in particular, copolymers consisting predominantly of ethylene with a small mole fraction of an alpha olefin comonomer, which introduces short-chain branches into the polyolefin molecule. In general, the need for a better technique for characterizing short-chain branching arises from the fact that certain mechanical properties, such as toughness and resistance to environmental stress cracking, are known to be sensitive to short-chain branch content for polyethylenes. Indeed, these properties seem to optimize at short-chain branch content values on the order of one percent or less, leading to the commercialization of ethylene copolymer grades in which such branches are deliberately introduced by incorporation of a comonomer such as vinyl acetate, butene-1, hexene-1, or octene-1.

The determination of this short-chain branch content, an important parameter governing the polymer properties required for the binary munitions storage application, has been a source of difficulty. Earlier studies² explored the use of wide angle X-ray scattering (WAXS) as a characterization tool for examining the branch content in polyethylene resins. Application of the WAXS method to this problem hinges on the fact that the branch points in the polyethylene can be incorporated as defects within the crystal structure of polyethylene, as shown in Figure 1. This has the effect of expanding the crystal lattice, particularly in the a direction, depending upon the amount of branch content in the resin.³⁻⁵ Precision measurement of the a lattice parameter is, therefore, potentially a means of characterizing branch content in the polymer molecule. Such a method is needed, especially in the regime of short-chain branches and low-branch content, where methods based on infrared absorption⁶ or molecular dimensions in solution⁷ become insensitive.

The infrared absorption method⁶ relies upon determination of the absorbance of a methyl band at 1378 cm^{-1} . This suffers from two shortcomings: (a) since even a linear polyethylene has methyl end groups, a correction (based on polymer molecular weight) is required to subtract out these end groups; and (b) the 1378 cm^{-1} band suffers from interference from nearby methylene group bands at 1368 cm^{-1} and 1352 cm^{-1} . Both effects result in reduced accuracy at low levels of branch content, the range of interest in the present application. Also, methods based on molecular dimensions⁷ are not useful for studying short-chain branching, which, unlike long-chain branching, has little effect on overall molecular dimensions. Short-chain branching is the important material parameter in the present context.

1. DISPER, C. R. *Characterization and Selection of Polymer Materials for Binary Munitions Storage*. U.S. Army Materials Technology Laboratory, AMMRC TR 83-45, August 1983.
2. DISPER, C. R. *Characterization and Selection of Polymer Materials for Binary Munitions Storage - Part 2: Characterization of LLDPE Resins*. U.S. Army Materials Technology Laboratory, AMMRC 84-28, July 1984.
3. WUNDERLICH, B., and POLAND, D. *Thermodynamics of Crystalline Linear High Polymers. II The Influence of Copolymer Units on the Thermodynamic Properties of Polyethylene*. J. Polym. Sci. A, v. 1, 1963, p. 357
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5. WUNDERLICH, B. *Macromolecular Physics*. Academic Press, New York, v. 1, 1973, p. 153-154.
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7. BILLMAYER, F. W., Jr. *Characterization of Molecular Weight Distributions in High Polymers*. J. Polym. Sci. C8, 1965, p. 161.

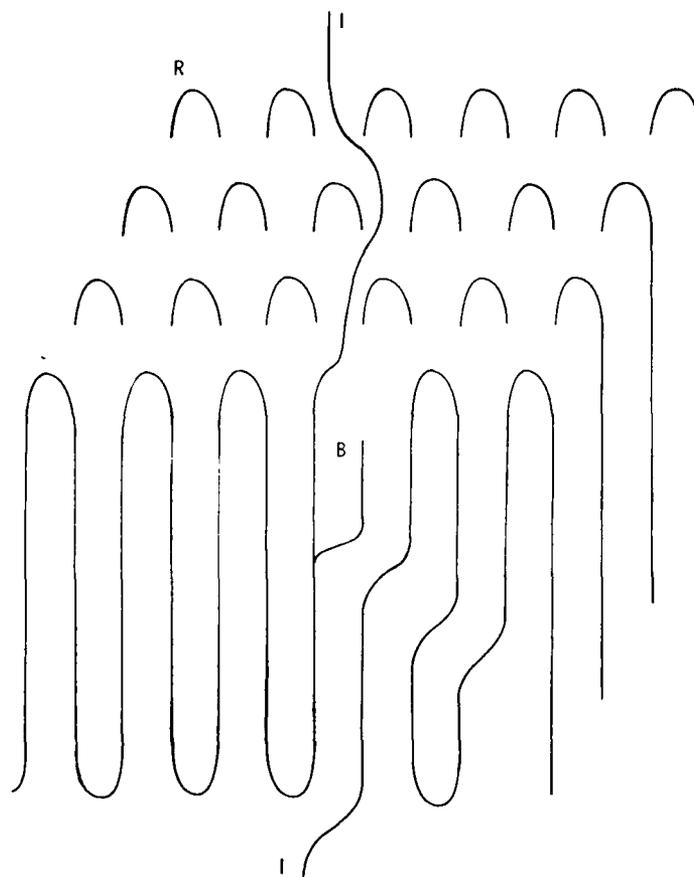


Figure 1. Branch point (B) incorporated inside a polyethylene-folded chain crystallite. R - regular folds and I - intercrystalline links.

Consequently, the possibility of characterizing such branch content by X-ray diffraction was explored² previously in this laboratory. The present work is a continuation of this effort, extending this work to a wider variety of candidate resins, and implementing the use of an improved X-ray diffraction method offering better precision and more rapid data acquisition.

Candidate Resin Samples

Candidate resin samples were supplied by Mr. Steven Kolodzey of the Chemical Research and Development Center, Aberdeen Proving Ground, MD, from resins and canisters from earlier studies at that location. Samples were available as either canisters fabricated for the storage of DF, or as sheet samples of the same resin sheets from which canisters were made. Table 1 reviews the history of these samples. The resins fall into four resin grades: (a) M407MQ, a polyethylene copolymer with a small amount of butene-1 comonomer originally used for DF containers in 1973; (b) M407MQ 687 PIP, a later production of M407MQ procured in 1977 under the indicated product improvement package (PIP) specifications; (c) M445, recommended by Phillips as a replacement grade for the now-discontinued M407MQ grade, with hexene-1 used in place of butene-1 as the comonomer; and (d) CL100, a crosslinking grade polyethylene homopolymer currently marketed by Phillips as a rotational molding resin.

Table 1. IDENTIFICATION OF CANDIDATE POLYETHYLENE RESIN SAMPLES

Polymer Type M407MQ	(1973 Polymer)
Canister 317 and 317: Fabricated and filled with DF in November - December 1973; opened and drained in 1981.	
Canister 182: Fabricated and filled with DF in November - December 1973; opened and drained in 1983. The polymer canister had a cracked burst disk.	
Polymer Type M407MQ 687 PIP	(1977 Polymer)
Canister 19HH: Stored in the horizontal position with DF for 18 months at 160°F as part of 687 PIP (Product Improvement Program)	
Polymer Type M445	(1982, 1983 Production)
Sheet 1982 production	
Sheet 1983 production; control sample for canister 140 (below)	
Canister 140: 1983 production; never filled with DF; stress relieved at 230°F for four days.	
Polymer Type CL100	(1982 Production)
Canister; no number, designated "CL100"	

The latter reportedly has excellent resistance to environmental stress cracking, but presents difficulties in that spin-welding to close to a filled canister cannot be accomplished due to the crosslinked character of the resin after molding.

EXPERIMENTAL PROCEDURES

Gel Permeation Chromatography (GPC) Procedures

Molecular weight characterization was accomplished using the Waters model 150-C gel permeation chromatograph. The polymer specimens were dissolved in trichlorobenzene and run at 135°C. Data were analyzed against known calibration standards using an on-line microprocessor.

Wide Angle X-Ray Scattering (WAXS) Procedures

Instrumentation - The X-ray diffraction unit used in this study incorporates advanced instrumentation techniques for rapid measurement of X-ray diffraction patterns. The performance of this instrument, which incorporates a position-sensitive X-ray detector and a microcomputer, has been reported in a recent publication.⁸ The important features of the instrument are summarized in Table 2. The position-sensitive proportional counter incorporated in this instrument operates similar to those described by Schultz⁹ and by Borkowski and Kopp.¹⁰

The rapid X-ray diffraction system measures intensity versus 2θ patterns by placing the detector with its sensitivity axis positioned parallel to the plane of the diffractometer (see Figure 2). As shown in Figure 2, the detector sensitivity axis z is coplanar with both the incident beam and the diffracted beam, with its

8. DESPER, C. R. *An Advanced Technique for Characterization of Polymer Materials by Wide Angle X-Ray Scattering in Materials Characterization for Systems Performance and Reliability*, eds., J. W. McCauley and V. Weiss, Plenum Press, New York, 1986, p. 319-337.
9. SCHULTZ, J. M. *Rapid Small-Angle and Wide-Angle X-Ray Studies of Crystallization Behavior in Polymers* J. Polym. Sci. Polym. Phys. Edn., v. 14, 1967, p. 2291.
10. BORKOWSKI, C. J., and KOPP, M. K. *Design and Properties of Position-Sensitive Proportional Counters Using Resistance-Capacitance Position Encoding*. Rev. Sci. Instr., v. 46, 1975, p. 951.

centerline positioned at a diffraction angle of $2\theta_0$. Each X-ray photon results in an analog pulse proportional in amplitude to its linear position, z , along the detector sensitivity axis, measured from the centerline, which translates into a diffraction angle 2θ measured from the centerline, which translates into a diffraction angle 2θ according to:

$$2\theta = 2\theta_0 + \tan^{-1}(z/L), \quad (1)$$

where L is the perpendicular distance from the center of the diffractometer to the detector axis. In the present work, data are accepted over a range of 14° in 2θ , which maps into 714 channels in the Lecroy 3500 multiple channel analyzer, thus, recording data at approximately 0.02° intervals. (The angular range may be increased, with a corresponding increase in the angular width of each channel, by reducing the working distance L .)

Table 2. WIDE ANGLE X-RAY DIFFRACTION SYSTEM

1. Picker Model 6238H X-Ray Generator
2. Picker Model 3645 Four-Circle Diffractometer
3. Technology for Energy Corporation Model 210 Position-Sensitive Proportional Counter
4. Ortec Nim Bin Electronics
 - a. Model 446A High Voltage Supply
 - b. 2 ea Model 575 Shaping Amplifiers
 - c. 3 ea Model 551 Timing Single Channel Analyzers
 - d. Model 433A Dual Sum and Invert Amplifier
 - e. Model 457 Time to Amplitude Converter
5. Lecroy 3500 Microcomputer
 - a. Model 3511 ADC Input Channel
 - b. Multiple Channel Analyzer Firmware in ROM
 - c. Intel Model 8080 CPU with 65k RAM
 - d. Flexible Disk I/O
 - e. Fortran and Basic Programming Systems Available

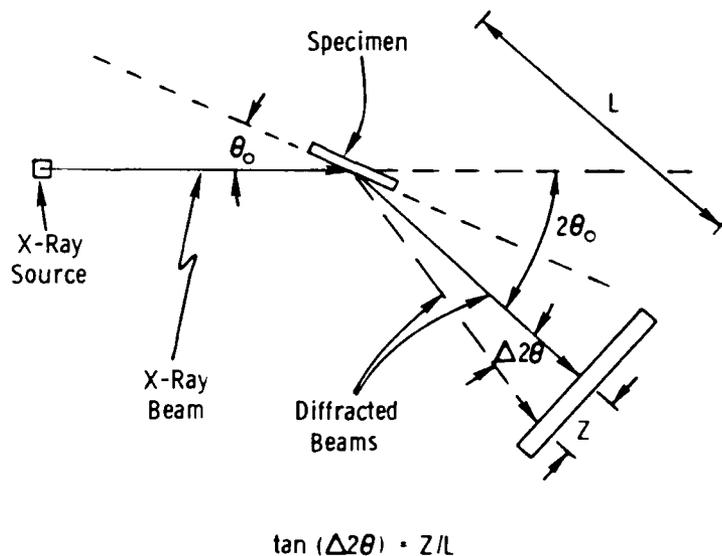


Figure 2. Experimental arrangement for measurement of 2θ pattern.

Calibration - In order to correlate branch content with crystal lattice parameters, calibration samples of known branch content are required. A series of polyethylene resins which have been extensively studied in the past was chosen. These samples, made available to the polymer science community in the 1960's by the Plastics Department of E. I. DuPont de Nemours & Co., Inc., are labeled "University Contact Polyethylene" and are numbered PE-75, -76, -78, -79, -80, -81, -82, and -85. Characterization data are available in the work of Bodily and Wunderlich.⁴ Except for the last one, these resins have density values in the 0.91 to 0.92 g/cm³ range and are termed low density polyethylenes. The final sample of this series, PE-85, along with two other resins, Marlex 6007 (Phillips Petroleum) and Chemplex 6109, served as standards of essentially linear polyethylene content. All of the standard samples were obtained as pellets and were compression molded at 170° to films of 0.2-mm thickness. Data for the branch content of the low density polyethylenes, as determined by the infrared method,⁶ were available; the high density resins were assumed from their method of polymerization and from their density values in the 0.95 to 0.96 g/cm³ range to be free of branching. The density, crystallinity, and branch content of the reference samples are given in Table 3.

Table 3. DATA FOR CALIBRATION SAMPLES OF POLYETHYLENE

Sample Designation	Density (g/cm ³)	Crystallinity,*	Branch Content [†]
PE-75	0.9143	0.44	1.7
PE-76	0.9211	0.43	2.1
PE-79	0.9219	0.49	2.2
PE-80	0.9213	0.49	1.8
PE-85	0.9512	0.69	0.0
6007	0.9532	0.70	0.0
6109	0.9620	0.76	0.0

*From density

†By infrared method

X-Ray Diffraction Procedural Details - The DF container samples for which branch content data are needed were available as cylindrical containers (canisters) of wall thickness 1.5 and 6 mm, and as thick sheets of the same thickness values. These specimens were prepared for X-ray studies by microtoming a section of 0.2-mm thickness, which was subsequently heat-relaxed by melting briefly on a glass microscope slide resting on a hot plate at 170°C. These, and the standard samples, were then further prepared by applying a very thin coating of graphite powder to one surface. To apply the graphite, the surface was first sprayed with a clear laquer (Illinois Bronze, Federal Stock No. 8010-515-2487), then dusted with graphite powder. The graphite powder provides an internal reference line in the X-ray diffraction pattern, namely the strong and sharp graphite (002) line. Earlier work in this laboratory² has shown the value of this internal reference line for improving the accuracy of the lattice parameter determination.

X-Ray Diffraction: Precision and Accuracy - The PSPC pattern for one of the graphite-coated standard polyethylenes is shown in Figure 3, along with three regions of interest from the pattern showing the three diffraction peaks observed. The microcomputer finds these peaks by a peak-search algorithm, then calculates the precise peak position by locating negative-going zero crossings in the first derivative of the data. (In contrast, the method used previously² for determination of peak

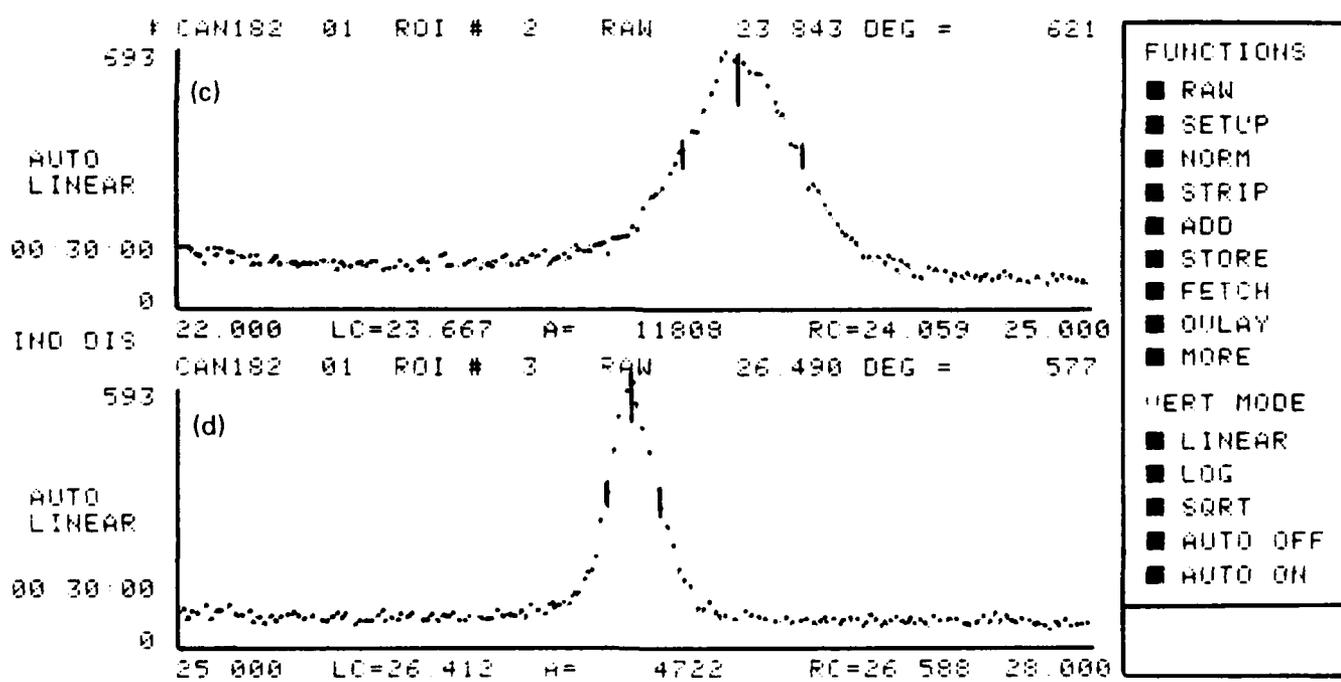
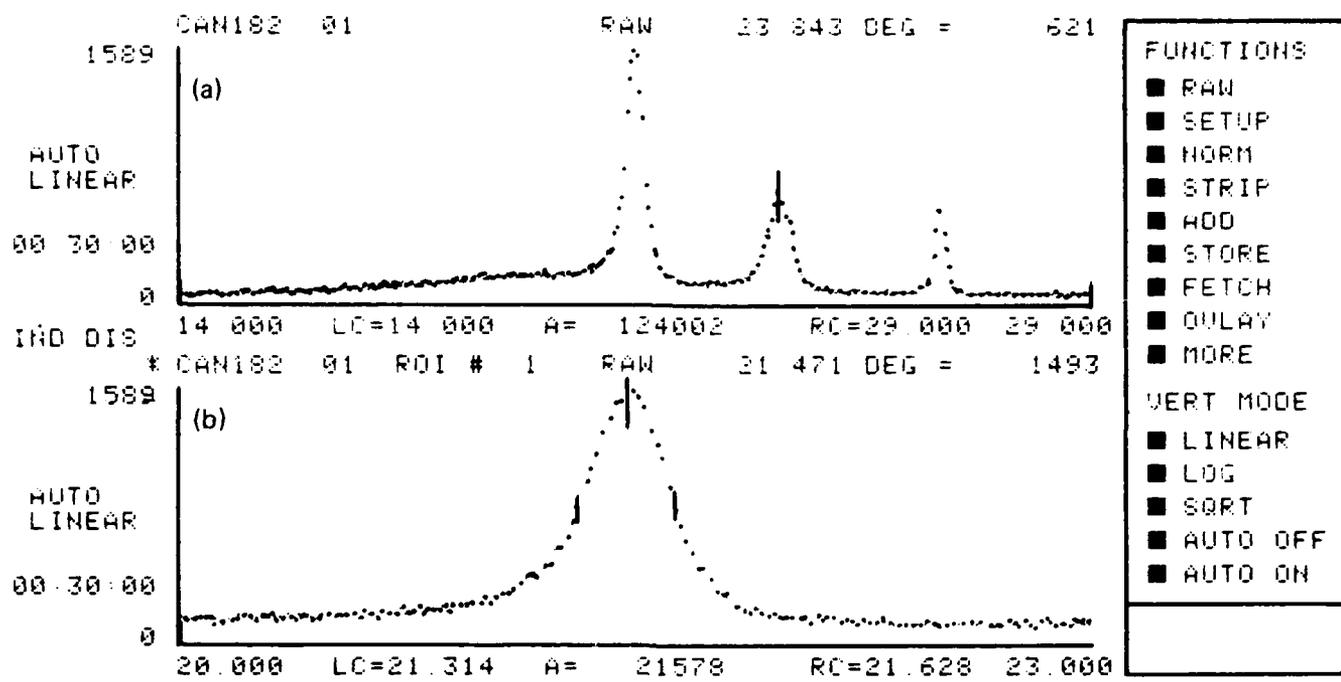


Figure 3. WAXS 2θ pattern of polyethylene sample from Can No. 182 using PSPC method: (a) entire pattern; (b) region of polyethylene (110) peak; (c) region of polyethylene (200) peak; and (d) region of graphite (002) peak.

position relied upon visual inspection of the intensity curve, and was precise to no better than 0.5 channels, or 0.01° . Determination with replicate data sets have shown the zero crossings of the first derivative method to be much more precise, as will be shown later in this section.) The microcomputer also applies a background correction, and determines the breadth and area of each peak, but these quantities are not of interest in the present case. A precise value for the \underline{a} lattice parameter of each specimen is obtained using the position of the polyethylene (200) peak with respect to the graphite (002) internal standard, which is assigned a 2θ value of 26.576° , corresponding to a \underline{d} spacing of 3.354 Å. This procedure compensates for any instrumental drift or misalignment, and results in a precision of 0.00005 Å in the polyethylene \underline{a} lattice parameter value, as determined by replicate measurements on a single specimen.

The temperature of the specimen is a second factor limiting the accuracy of determination of branch content from measurement of the \underline{a} axis lattice parameter. No specimen temperature control was employed in the present instrument, so the specimen temperature was identical with room temperature and subject to variations inherent in the air conditioning system. Measurement of the polyethylene \underline{a} parameter as a function of temperature in the range of 22°C to 28°C for two resins (see Figure 4) yielded an expansion coefficient $\underline{d}\underline{a}/\underline{d}T$ of 1.92×10^{-3} and 2.22×10^{-3} Å/°C. (There is a possibility of dependence of this expansion coefficient upon branch content.) For valid values of the \underline{a} parameter, subsequent data were corrected to a reference temperature of 25°C , using a nominal expansion coefficient of 2.0×10^{-3} Å/°C.

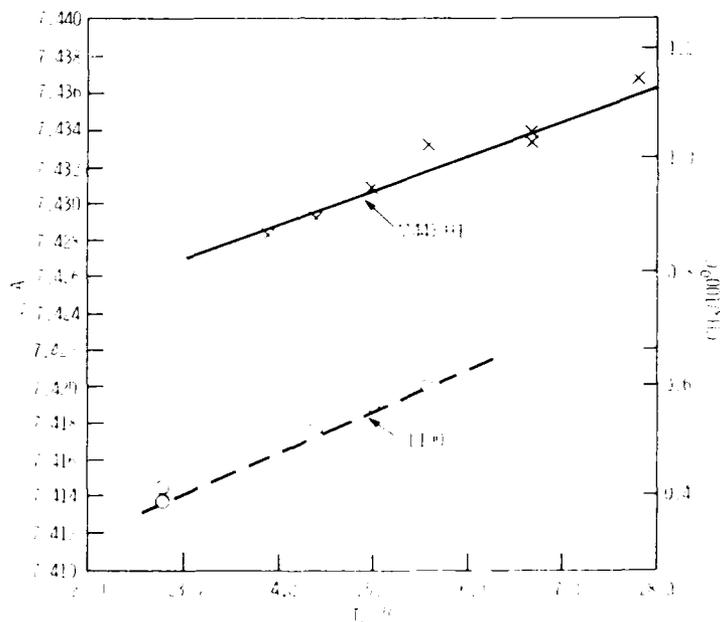


Figure 4. Effect of temperature upon \underline{a} lattice parameter and apparent branch content.
(X) - resin M445, canister 140 (solid line); (O) - resin CL100 (dashed line).

To assess the accuracy of the \underline{a} lattice parameter determination, including the effect of normal temperature fluctuations in an air conditioned room, replicate determinations were made with a single resin specimen at a room temperature of 75°F , or 23.9°C . The results (see Table 4) show a standard deviation of 0.0002 Å for the \underline{a} parameter, which propagates into a standard deviation of 0.01 (CH₃/100C) in the

branch content. Table 4 also demonstrates that the graphite standard is essential to obtaining this level precision: the standard deviation in the raw polyethylene (200) Bragg angles is 0.0046°, but reduces to 0.0007° when corrected by reference to the graphite internal standard.

Table 4. REPLICATION OF BRANCH CONTENT MEASUREMENT FOR M445 SAMPLES

Sample: Resin M445, 1983 Sheet, Control for Heat-Treated Can No. 140					
	2θ , Raw*	2θ , Corr'd*	$d(200)$, Å	a , Å	Apparent (CH ₃ /100C)
	23.880 ₃	23.975 ₅	3.7115 ₆	7.4231 ₂	0.697
	23.875 ₃	23.976 ₂	3.7114 ₅	7.4229 ₀	0.690
	23.873 ₉	23.974 ₂	3.7117 ₆	7.4235 ₂	0.711
	23.868 ₉	23.975 ₅	3.7115 ₆	7.4231 ₂	0.698
	23.867 ₇	23.974 ₇	3.7116 ₈	7.4233 ₆	0.706
Mean Value	23.873 ₂	23.975 ₂	3.7116	7.4232	0.70 ₁
Std. Devn.	0.004 ₆	0.0007	0.0001	0.0002	0.010

The a lattice parameter values were obtained for the seven reference samples of Table 3 and for eight polyethylene samples of unknown branch content. Using the infrared values for branch content for the reference samples, a linear regression line was obtained (Figure 5) relating branch content to the a lattice parameter. The regression line was then used to evaluate the branch content of the unknown samples, plotted as circles in Figure 5. The branch content of the unknowns may be read from the corresponding ordinate values in Figure 5, or may be calculated from the equation of the regression line:

$$(\text{CH}_3/100\text{C}) = 33.03 (a - 7.4020). \quad (2)$$

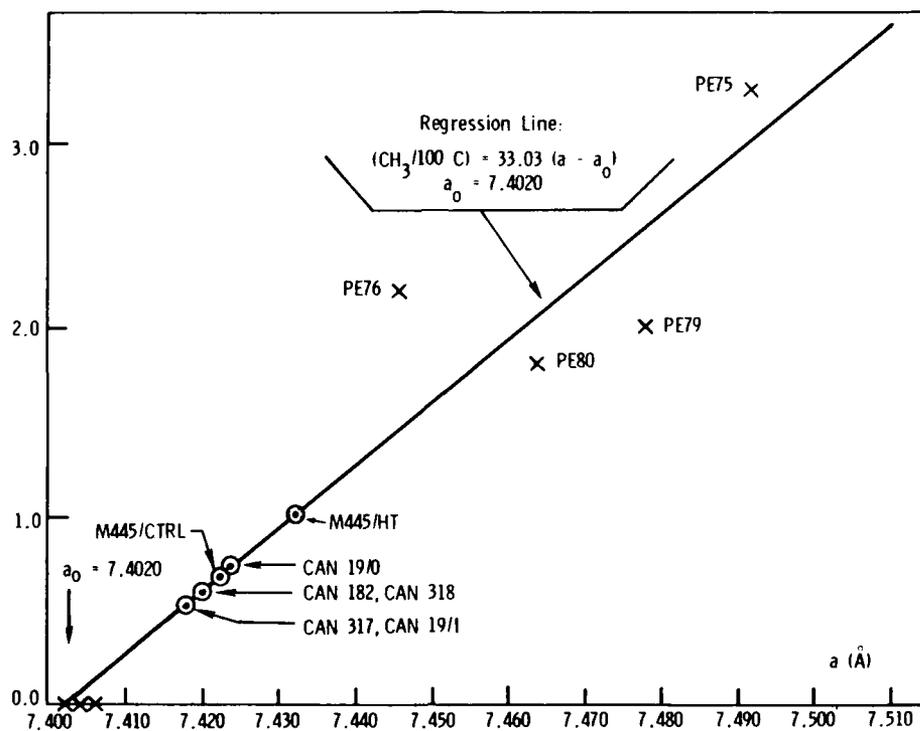
Density Determinations

Polymer densities were determined in a density gradient column at 23°C, using glass beads of known density for calibration. To obtain crystallinity values, limiting values of amorphous and crystalline specific volumes V_A and V_C of 1.170 and 0.999 cm³/cm were used, based on the data of Gopalan and Mandelkern.¹¹

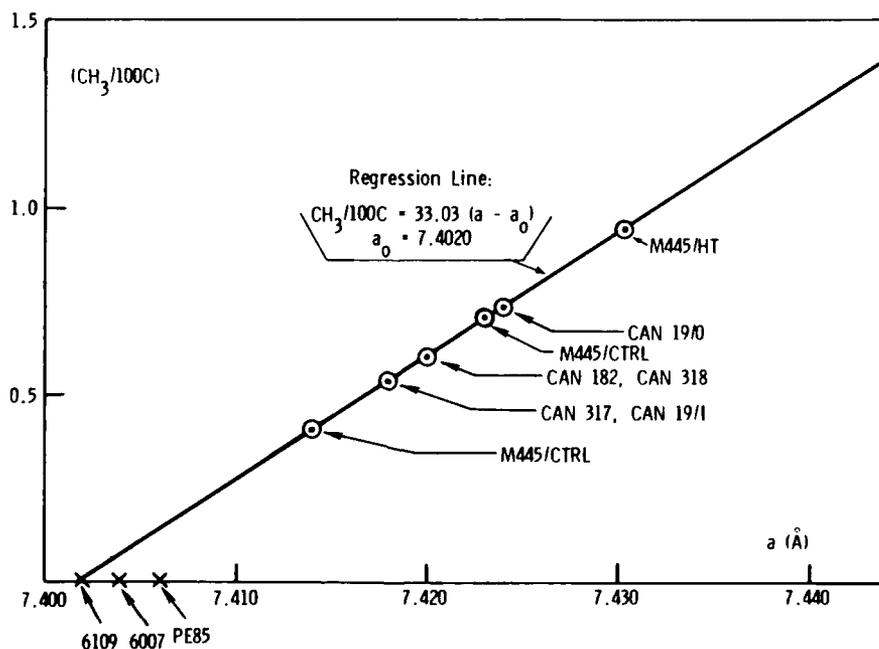
RESULTS

The results of the molecular weight characterization by GPC are summarized in Table 5. It must be pointed out that the CL100 resin sample was found to have been only partially soluble in trichlorobenzene. Further investigation revealed this to be a crosslinking grade of polyethylene, which had undergone a chemical crosslinking reaction during the rotational molding process. The GPC results of the soluble portion of resin CL100 are included in Table 5 for completeness, but are not a useful characteristic of the whole resin, which effectively has an infinite molecular weight.

11. GOPALAN, M. R., and MANDELKERN, L. *Degree of Crystallinity of Linear Polyethylene from Wide-Angle X-Ray Diffraction*. Polymer Letters, v. 5, 1967, p. 925.



a. Full range of data including standards (X)



b. Detail of data for unknowns (O)

Figure 5. Linear regression correlation: polyethylene branch content versus a ; solid line is least squares fit.

Table 5. POLYETHYLENE MOLECULAR WEIGHT CHARACTERIZATION
BY GEL PERMEATION CHROMATOGRAPHY

Resin	Can Number	Year	$\bar{M}_n^{\#}$	$\bar{M}_w^{\#}$	$\bar{M}_z^{\#}$	\bar{M}_w/\bar{M}_n
M407MQ	182/X*	1973	23,000 (8.7%)	183,000 (1.5%)	420,800 (1.3%)	7.8
M407MQ	317/O*	1973	28,300 (6.8%)	168,400 (1.7%)	445,300 (2.4%)	6.0
M407MQ (repeat)	317/O*	1973	29,400 (5.2%)	166,700 (2.4%)	429,400 (2.8%)	5.7
M407MQ	317/I*	1973	22,300 (10.6%)	136,000 (5.6%)	391,300 (5.7%)	6.1
M407MQ	318/X*	1973	27,600 (3.9%)	168,000 (1.8%)	444,400 (2.4%)	6.1
M407MQ (687 PIP)	19/O*	1977	19,100 (5.0%)	147,300 (0.9%)	343,200 (2.3%)	7.7
M407MQ (687 PIP)	19/I*	1977	15,300 (3.2%)	118,200 (2.1%)	294,100 (3.4%)	7.7
M445	Sheet	1982	22,600 (1.6%)	162,900 (1.1%)	367,100 (1.6%)	7.2
M445 (repeat)	Sheet	1983	22,200 (5.0%)	169,600 (0.2%)	392,800 (0.5%)	7.6
M445/HT	140	1983	19,400 (12.6%)	176,900 (1.3%)	426,300 (1.2%)	9.2
CL100 (Sol Fraction) [†]	No Number	1983	10,600 (10.9%)	57,500 (3.3%)	178,000 (4.7%)	5.5

*/I=sampled at interior surface, /O=sampled at exterior surface, /X=sampled at cross section. Cross section sample used if not otherwise indicated.

[†]For CL100 rotationally molded specimen, made from a crosslinking resin, only 20% to 30% of the polymer could be dissolved. Values apply only to the soluble fraction.

[#]Quantities in parentheses are the estimated error (standard deviation) of the individual molecular weight determinations.

Table 6 shows a comparison of the present GPC results with past determinations in three instances where GPC results for the same specimen are available from previous studies^{1,2} in this series. The results show a remarkable consistency in this type of determination, particularly for comparisons 1 and 3 (M407MQ, can #317, outer sidewall; and M445, 6-mm thick sheet). In these cases the comparisons for \bar{M}_n , \bar{M}_w , and \bar{M}_z are all well within the indicated error limits of the determinations. In comparison 2, however, the resin (M407MQ, can #318) tested out lower in \bar{M}_n and \bar{M}_z , in the first case within the high error brackets of that particular determination, but in the case of \bar{M}_z , differing by more than the small error brackets of that determination. This result, however, is attributable to differences in the sampling method: the reference¹ determination was from a sample shaved from the sidewall exterior of the canister, while the present data are from a sample shaved from an interior cross-section surface. This difference in molecular weights is real and can be explained by the different shear history experienced at these two positions: resin at the exterior surface underwent high shear while passing through the pipe extrusion die, and suffered some breakdown in molecular weight, while the resin at the interior of the sidewall passed through the die under neutral shear conditions. In all, the results of Table 6 point up (a) the accuracy of the GPC determination, and (b) the need to take sampling method into consideration for high reproducibility.

Table 7 lists the results of the density determinations, along with the corresponding crystallinity values; and the branch content values as determined by X-ray diffraction from the a lattice parameter values. Since two of the branch content determinations in this report were made for resins for which branch content was earlier measured² by X-ray diffraction, the results for these samples are compared

Table 6. COMPARISON OF PRESENT DATA WITH PAST GPC RESULTS

Comparison 1. Resin: M407MQ; Production: 1973; Can: #317;					
Sampling: outer surface of sidewall.					
Source of Data	\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_w/\bar{M}_n	Remarks
Reference (1)	27,300 (14.4%)	167,400 (1.9%)	435,400 (1.8%)	6.1	
Present Work	28,300 (6.8%)	168,400 (1.7%)	445,300 (2.4%)	6.0	Determination #1
Present Work	29,400 (5.2%)	166,700 (2.4%)	429,400 (2.3%)	5.7	Determination #2
Comparison 2. Resin: M407MQ; Production: 1973; Can: #316;					
Sampling: as indicated; differs for the two determinations.					
Source of Data	\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_w/\bar{M}_n	Remarks
Reference (1)	23,900 (19.9%)	159,200 (1.4%)	415,500 (1.6%)	6.7	Sidewall exterior
Present Work	27,600 (3.9%)	168,000 (1.8%)	444,400 (2.4%)	6.1	Sidewall, cross section
Comparison 3. Resin: M445; Production: 1982; 6-mm thick sheet.					
Source of Data	\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_w/\bar{M}_n	Remarks
Reference (2)	22,200	163,400	370,000	7.4	
	23,100	161,700	367,000	7.0	
Present Work	22,600 (1.6%)	162,900 (1.1%)	367,100 (1.6%)	7.2	

Note: Entries in parentheses are standard deviations of five determinations corresponding to the entry above them in the table. No standard deviations are available for the Reference (2) work; each of the two entries represents, in that case, a single determination rather than an average of five.

Table 7. POLYETHYLENE BRANCH CONTENT FROM LATTICE PARAMETER MEASUREMENTS USING X-RAY DIFFRACTION

Resin	Density (g/cm ³)	X _C (w/w)	Can Number	Year	a (Å)	Branch Content (CH ₃ /100C)
M407MQ	0.9395	0.618	Sheet	1973	7.430	0.92
M407MQ	N/A	N/A	182	1973	7.420	0.60
M407MQ	0.9381	0.608	317	1973	7.418	0.54
M407MQ	0.9408	0.626	318	1973	7.420	0.60
M407MQ--687 PIP	0.9420	0.624	Sheet	1977	7.426	0.80
M407MQ--687 PIP	0.9436	0.645	19/O*	1977	7.424	0.73
M407MQ--687 PIP	N/A	N/A	19/I*	1977	7.418	0.54
M445	0.9426	0.638	Sheet	1983	7.423	0.70
M445/HT	0.9472	0.668	140	1983	7.431	0.95
CL100	0.9401	0.622	No Number	1983	7.420	0.60

* /O - specimen from outside of can; /I - specimen from interior of can.
Specimen taken from exterior surface if not indicated otherwise.

Correlation used:

$$(\text{CH}_3/100\text{C}) = 33.03 (a - a_0); a_0 = 7.402 \text{ \AA}$$

in Table 8. The earlier branch content determinations differ from the present values by 0.07 and 0.11 (CH₃/100C), consistent with the estimate of 0.12 (CH₃/100C) for the error in this determination in the earlier work.²

Table 8. COMPARISON OF PRESENT DATA WITH PAST BRANCH CONTENT MEASUREMENTS

Resin	Ref. (2) Results		Present Results	
	a	(CH ₃ /1000)	a	(CH ₃ /100C)
M407MQ	7.432	0.85	7.432	0.92
M407MQ-687 PIP	7.434	0.91	7.426	0.80

DISCUSSION

The results indicate that there is little significant difference among the three extrusion grade resins--M407, M407MQ (687 PIP), and M445 in terms of either molecular weight distribution or branch content. M407MQ (687 PIP) appears to be somewhat lower than the other two in all three averages (\bar{M}_n , \bar{M}_w , and \bar{M}_z). The heat treated sample, M445/HT, shows a lower \bar{M}_n , and a higher \bar{M}_w and \bar{M}_z than its control sample. Since the former is most sensitive to short molecules, while the latter two are most sensitive to long ones, this suggests that the heat treatment broadened the molecular weight distribution slightly. All in all, however, the differences in molecular weight characteristics are too small to have a significant effect on expected performance.

The three are all comparable in terms of crystallinity.

Examining the data in Figure 5 and Table 7, it is seen that the branch content values for the candidate resins range from 0.5 to 1.0. The level of variability within a given resin type is considerable. For instance, M407MQ yields values of branch content of 0.92, 0.60, 0.54, and 0.60; a range which brackets the values for all other resins. The differences between resin grades is, consequently, of less significance than the differences within a resin grade for branch content. Such differences within a resin grade probably reflect some inhomogeneity in the polymerized resin, or differences in processing history, but may be small enough to be acceptable in terms of properties of the finished product. In the one case, where a definite comparison of post-polymerization history is possible, i.e., M445 versus M445/HT (the latter having been subjected to an extreme heat treatment of 230°F for four days), the values observed for branch content, 0.70 and 0.95, respectively, are definitely different in terms of experimental accuracy. However, the heat-treated branch content value is 0.95 is close enough to the range observed for the other resins that the heat treatment may be said to have had no drastic effect upon the branch content.

At present, however, the degree of sensitivity of materials properties to branch content in this range is not known, so the allowable tolerance in this materials characteristic is also unknown.

The higher value for the one heat-treated resin (M445/HT) may arise from a small degree of chain oxidation, leading to the incorporation of carbonyl groups into the polyethylene crystallites. As an alternative hypothesis, the prolonged

annealing could well have caused thickening of the lamellar polyethylene crystallites, which has been shown by Davis and coworkers¹² to have an effect on the lattice parameters. This hypothesis is not believed to have been responsible for the higher apparent branch content of M445/HT for two reasons: (a) all specimens were melted and recrystallized on a glass slide, which should have removed all memory of the previous crystalline morphology; and (b) the hypothesized effect was in the wrong direction, since thicker crystallites have smaller lattice parameters.

In terms of molecular weight values, high molecular weights are desirable to maximize expected mechanical properties of the final product. The results in Table 5 show all three candidate extrusion resins (M407MQ, M407MQ--687 PIP, and M445) to be roughly comparable in terms of their molecular weight characteristics, with some variability, which most likely results from differences in processing history. Certainly, no resin can be singled out as being deficient in this regard. For the cross-linking resin, CL100, such a comparison is not valid, of course; cross-linking results in an essentially infinite molecular weight, but renders the product unuseable because of the previously discussed sealing problems.

In terms of the method of characterization of branch content, the greatest area for improvement is in the standard samples. The X-ray lattice parameter method has the advantage of speed, precision, and simplicity for work in this area, but does not, of itself, give an absolute measure of branching. Standards are needed over a wide range of branch content values, not just at the low and high ends, to test for curvative in the correlation between branch content and lattice parameter. This has not been possible in the past because a better method was needed for establishing the branch content of the standards. C-13 nuclear magnetic resonance could fill this need, and such instruments are becoming more widely available. When such characterized standards become available, the X-ray lattice parameter method may be put on a more solid absolute basis. Even lacking a wide variety of accurate standards, the lattice parameter method for measuring branch content is valuable in terms of giving precise comparisons of various resins.

CONCLUSIONS

The replacement resin grade M445 appears to be equivalent in terms of characteristics expected to affect final product performance to the earlier grades, M407MQ and M407MQ--687 PIP, previously qualified for this application. Nonetheless, it is in the government's interest to continue to look for acceptable grades from competitive suppliers.

The determination of branch content in polyethylene resins has been rendered more rapid and precise by the microcomputer method employed in the present work. The greatest opportunity for improvement in accuracy (as opposed to precision, or reproducibility) is in the area of the standard samples. Standards are needed which (a) cover a wider range of branch content values, and (b) have been characterized for branch content themselves by a method better than infrared absorption, such as C-13 nuclear magnetic resonance. (C-13 nuclear magnetic resonance does afford a more direct and more accurate determination of short-chain branching, even offering information as to the length of the branches, but is too elaborate and time consuming

12 DAVIS, G. L., WEEKS, J. J., MARTIN, G. M., and FBY, R. K. *Cell Dimensions of Hydrocarbon Crystals - Surface Effects*. J. Appl. Phys., v. 45, 1974, p. 4175.

for many routine types of analysis.) Nonetheless, the present X-ray correlation method, offering good precision but undetermined accuracy because of the standardization problem, gives valid comparisons between resins.

Gel permeation chromatography (GPC), now also known as size exclusion chromatography (SEC), is a valuable method for characterization of polymer molecular weight, and has proven very useful for monitoring polymer grades to assure consistency in polymer properties.

RECOMMENDATIONS

The following is recommended:

1. Acceptance of M445 as a replacement for the previously qualified M407MQ grade for use in DF canisters.
2. Continued screening of competitive polymer grades as alternatives for this application.
3. Inclusion of GPC characterization in the specifications for polyolefin resins for this application.
4. Further exploration of the X-ray diffraction method with the aim of establishing a standard method of branch content determination, particularly for LLDPE polymers, where short-chain branching is a key factor controlling properties.

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The author also wishes to thank the Plenum Publishing Corporation for permission to reproduce Figures 1, 2, 3, and 5, and Tables 2, 3, and 7, which originally appeared in Reference 8.

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1 Author

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CHARACTERIZATION AND SELECTION OF POLYMER
MATERIALS FOR BINARY MUNITIONS STORAGE
PART 3: BRANCH CONTENT DETERMINATION
C. Richard Desper

Technical Report MT, TR 7-77, September 1977, 11 pp.
Classification: UNCLASSIFIED
AMMS Code 6176-2553A11

Previous studies of potential failure mechanisms in polymer containers for binary munitions have established that good environmental stress cracking resistance is an essential property of a successful candidate. This study reports that it is also found that the linear low density polyethylene (LLDPE) offered performance advantages, and that the key resin component of LLDPE is the extent of short-chain branching. A characterization method which includes a ring proton lattice parameter determination for correlation with the degree of branching has been implemented. The data acquisition method obtains the required wide angle X-ray scattering (WAXS) data at greatly enhanced speed, without the need for any data reduction. The data acquisition system combines a position-sensitive X-ray detector with a 65 kilobyte microcomputer capable of operating as a multi-channel analyzer and of performing immediate data analysis. The method is applied to the determination of branch content in a series of polyethylene resins for binary munitions storage. In addition, the resins are characterized and compared in terms of crystallinity and molecular weight distribution.

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