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THE USE OF RADIATION-INDUCED PLASTIC MEMORY TO DEVELOP NEW SPACE ERECTABLE STRUCTURES

Contract NASr-78 with
The National Aeronautics and Space Administration

Final Report

George Odian
Bruce S. Bernstein

April 15, 1963

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CR-50,447

FOREWORD

The work described in this report was performed under Contract NASr-78, entitled "The Use of Radiation-Induced Plastic Memory to Develop New Space Erectable Structures," with the National Aeronautics and Space Administration.

The authors wish to acknowledge the assistance of Mr. James J. Kelly for the performance of the degree of restoration determinations and the majority of the restoring force measurements. The assistance of Messrs. Thomas A. Mann and Elliot Ratchik in performing some of the restoring force measurements and fruitful discussions with Mr. Maurice Keesing are also acknowledged.

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1.0 INTRODUCTION

1.1 Nature of Polyethylene

Polyethylene, like other polymers, is a high molecular weight compound built up by the repetition of small monomer units. An introduction to the preparation and properties of polyethylene can be found in the texts by Billmeyer[1] and Golding.[2] More comprehensive and detailed information is available in the text by Raff and Allison.[3]

Polyethylene is prepared by the addition polymerization of ethylene:

$$n\ CH_2{=}CH_2 \longrightarrow (-CH_2-CH_2)_n$$

In general, two different processes-one a high pressure and the other a low pressure process-are employed for ethylene polymerization. The high pressure technique proceeds via a free radical process and requires pressures of 1000-3000 atmospheres or higher and temperatures as high as 250°C. Polyethylenes synthesized by the high pressure process are low density (ca. 0.91-0.92) polyethylenes possessing 60-70% crystallinity. The low pressure polyethylene process proceeds via an ionic mechanism at considerably lower pressures (30-100 atmospheres) with the use of various catalysts such as those of the Ziegler type. The low pressure process yields high density (ca. 0.95-0.96) polyethylene possessing 80-90% crystallinity.

A wide variety of monomers can be made to copolymerize with ethylene at high pressures. Among these are ethyl acrylate and vinyl acetate.

$CH_2{=}CH{-}COOC_2H_5$	$CH_3{-}COO{-}CH{=}CH_2$
ethyl acrylate	vinyl acetate

Copolymers of ethylene with alpha olefins such as butene-1 can be prepared by the techniques used in making linear polyethylenes.

$$CH_2{=}CH{-}CH_2{-}CH_3$$

butene-1

1.2 Structure of Polyethylene

Low and high density polyethylenes differ quite markedly in their properties. For example, high density polyethylene has higher tensile strength and crystalline melting point (135°C. vs. 110°C.). The differences between high and low density are due in large part to the different degrees of chain branching present in the two. Chain branching has a predominant effect on the degree of crystallinity and therefore on the density and other properties of polyethylene.

Low density polyethylene is highly branched (ca. 1-4 branches per 100 carbon atoms) while high density polyethylenes are considered to be "linear". High density polyethylenes of density 0.96 possess less than 0.1 branches per 100 carbon atoms.

The type of branching that occurs is of two types-long chain and short chain. Long chain branching is due to the intermolecular chain transfer to "dead" polymer which normally occurs during propagation. Short chain branching occurs by intramolecular chain transfer. The number of long chain branches per molecular in typical polyethylenes are much less than the number of short chain branches (ca. 1:50).

Like any semi-crystalline polymer, polyethylene consists of both crystalline and amorphous regions. The crystalline regions consist of chain segments lined up so that inter-chain attraction occurs. These crystallites, in turn, are aligned into larger ordered regions called spherulites. Spherulites consist of a large number of crystallites radiating in all directions from a single point. Many factors (molecular weight, chain branching, rate of cooling from the melt, etc.) are involved in the number and size of crystallites and spherulites that are present in polyethylene. The exact nature of the structure of polyethylene is still the subject of much discussion. Current thought is based on the "folded-chain" theory of crystallinity.[4,5]

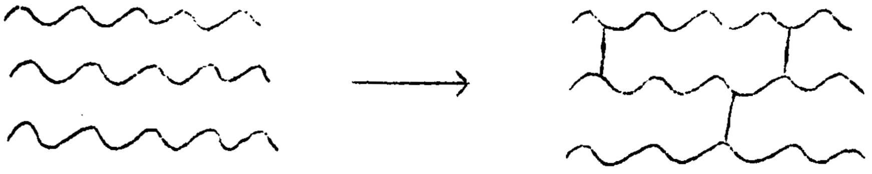
When polyethylene is heated, as with any crystalline compound, the ordered regions are destroyed. With a simple pure crystalline compound, melting occurs at a sharply defined temperature. Polyethylene, like other polymers containing crystalline and amorphous regions, does not melt at a sharply defined temperature; with rise of temperature, the proportion of amorphous material increases until all the crystalline regions are melted. There is a gradual diminution in the proportion of crystalline material from room temperature upward with an increased rate of diminution as the polymer approaches the final melting point.

When a polyethylene specimen is heated to melting and then cooled, recrystallization of the melt occurs. The nature of the crystalline state which occurs on recrystallization may or may not be similar to that which existed originally in the polymer; this will depend upon many factors (e.g., temperature, rate of cooling, etc.) and is discussed in the literature.[1,3] In any event, crystal growth starts anew on cooling and no remnants of the original crystallite/spherulite arrangements remain.

Cooling of a polymer specimen heated to some temperature below T_m presents a different situation. Such a specimen contains both melted and unmelted crystalline regions; cooling results in recrystallization of the melted regions. Crystalline regions formed from the melt are now present along with the remnants of those which never melted. The exact nature of these two crystal types, having different previous histories, does not concern us at present. Nor are we concerned at this time whether or not the presence of crystalline region affects the nature of the crystals forming from the melt. It is, however, very important to keep in mind that polyethylene heated to T_m or above and cooled will be different in nature from polyethylene heated to some temperature below T_m and cooled.

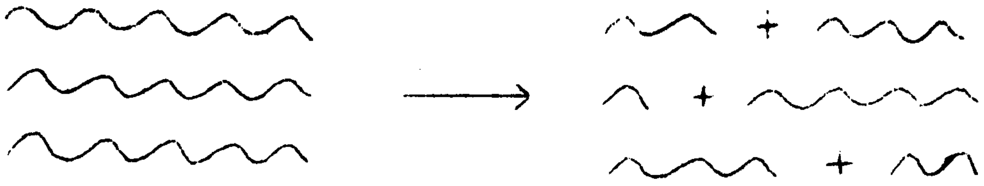
1.3 Effect of Ionizing Radiation on Polymers

Ionizing radiations, such as electrons from an accelerator or gamma rays from Cobalt-60, generally interact with polymeric materials to cause either crosslinking or degradation. (Other reactions, such as the production or removal of unsaturation and the formation of gases, may also occur.) Extensive discussions on the effects of radiation on polymers can be found in the texts by Charlesby[6] and Chapiro.[7] The overall effect of crosslinking is that the molecular weight of the polymer increases until ultimately a three-dimensional insoluble network is formed.



Crosslinked polymers no longer melt at the normal melting temperature, and have increased tensile strength and decreased elongation.

On the other hand, radiation degradation results in the polymer suffering random chain scissions.



Thus, the molecular weight steadily decreases with radiation dose and in extreme cases a low molecular weight liquid may result. Degradation results in the lowering of the tensile strength of a polymer.

Since both crosslinking and degradation occur simultaneously in most polymers, it is the relative tendencies toward the two reactions which determine the net result of irradiation. Thus, if crosslinking occurs at a higher yield than chain scission the net result is crosslinking whereas if chain scission is predominant, the polymer degrades. Polymers which crosslink upon irradiation include polyethylene, polypropylene, polystyrene, polyacrylates, polyvinyl chloride, polyamides and polyesters. Polymers which degrade upon irradiation include polyisobutylene, polymethacrylates, polyvinylidene chloride, polytetrafluoroethylene, polytrifluorochloroethylene and the cellulosics. (It should be mentioned that radiation techniques involving the use of polyfunctional monomers in conjunction with radiation reverse the normal course of degradation in many of the latter cases and result in crosslinking.[8])

The exact path by which radiation-induced crosslinking/scission reactions occur has been the subject of much discussion. The generally accepted mechanism involves the reaction of free radicals[9] although ionic mechanisms[10,11] have also been postulated. Furthermore, recent work on the irradiation of simple organic compounds allows one to postulate a mechanism for polymer crosslinking involving carbenes.[12]

1.4 Memory of Irradiated Polyethylene

Irradiated (crosslinked) polyethylene possesses the interesting property of elastic memory. At ambient temperatures, it is similar to the unirradiated polymer; however, above its normal T_m, irradiated polyethylene behaves as an elastomer. Thus, deformation of the polymer in the rubbery state will induce an elastic response; removal of this stress at the elevated temperature will be followed by recovery or relaxation.

However, if the polyethylene is cooled in the deformed state, crystallization will occur and result in a "locking-in" or retention of the deformed shape. If the deformed specimen is subsequently heated above the normal T_m of the polyethylene (i.e., crystalline melting), the restraints on the specimen's memory are removed and it restores to the shape it possessed during irradiation.

The elastic memory of irradiated polyethylene has been briefly referred to in the literature by Charlesby,[6] Lanza and Cook,[13] and Chapiro.[7] However, fundamental information regarding the parameters which effect and control this elastic memory is not available.

1.5 Scope of Work

We have performed, under Contract NASr-78 with the National Aeronautics and Space Administration, an exploratory study into the memory phenomenon. This study, although fundamental and empirical in nature, has been geared toward an understanding of methods that would allow adaptability of the phenomenon to possible use in erectable space structures. In principle, the memory effect should allow the preparation of compactly folded polymer shapes and structures which can be transported into space. By the application of heat (from the sun) after arrival, a predetermined shape and structure could be obtained.

This work has been geared to a study of

1. The magnitude of the restoration forces exerted by deformed polymers during the process of restoration to the undeformed (non-stressed) state.

2. The degree of completeness with which restoration (memory) occurs.

3. The conditions which are required to change the minimum temperature at which complete restoration can be effected.

The parameters which control these aspects of the memory effect and which were studied are

1. Polyethylene properties.
2. Radiation dose.
3. Deformation conditions.
4. Cooling (memory "locking-in") conditions.
5. Restoration conditions.

2.0 MATERIALS AND SAMPLE PREPARATION

2.1 Materials

Many polyethylene grades were studied during the course of this investigation. The polyethylene homopolymers and their properties are listed in Table 2.1. (Polyethylene and polyethylene-butene polymers are both referred to in this report as "polyethylene homopolymers.") Table 2.2 indicates the grades of Vexar polyethylene mesh studied, and their physical properties. Table 2.3 lists copolymers of ethyl acrylate or vinyl acetate with polyethylene which were used.

Table 2.1

Polyethylene Grades Evaluated for Memory Study

Grade[a]	Density (gm./cc.)	T_m (°C.)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	Melt Index
Alathon 14	0.915	108	22-26	800-1000	1.9
Alathon 15	0.915	111	15-20	500	4.0
Alathon 7010	0.955	132-135	15	160	0.5
Alathon 7030	0.955	132-135	13-14	105	3.0
Alathon 7040	0.957	132-135	11-12	88	6.0
Alathon 7511	0.960	132-135	15-20	150-175	0.3
Epolene E-10	0.940	105-110	-	2.5	Very High
Grex 50-025[b]	0.950	131-132	7.6	130	2.5
Grex 50-050[b]	0.950	131-132	6-7	70-80	5.0
Hi-Fax 1901	0.939	129-131	-	> 2000	ca. 0
Marlex 5003[b]	0.950	124	15-20	188	0.3
Marlex 6002	0.960	127	14	171	0.2

[a] The Alathon grades are manufactured by DuPont, Grex by W.R. Grace, Hi-Fax by Hercules, Epolene by Eastman Chemical, and Marlex by Phillips.

[b] These grades contain small amounts of butene-1 as copolymer. The Grex materials contain 2.5-3% and the Marlex ca. 5% butene-1.

Table 2.2

Vexar Mesh Polyethylene Evaluated for Memory Study

Grade[a]	Density (gm./cc.)	Thickness (mil)	Hole[b] Dimensions (cm.)	# Units per inch
D 1/1-100-90-PE-1	0.910-0.925	ca. 145	2.5	2
D 3/3-10-90-PE-1	0.910-0.925	60-85	1.0	3
D 8/8-30-90-PE-1	0.910-0.925	ca. 40	0.4	7
D 12/12-30-90-PE-2	0.926-0.940	ca. 50	0.3	10
D 4/4-30-90-PE-3	0.941-0.965	ca. 40	0.5	4
D 6/6-20-90-PE-3	0.941-0.965	ca. 25	0.5	6

[a] All materials are manufactured by DuPont

[b] Shape of holes = diamond

Table 2.3

Polyethylene Copolymers Evaluated for Memory Study

Grade[a]	Comonomer Composition	Melt Index	T_m (°C.)	Density (gm./cc.)
DPDB-6169	15% ethyl acrylate	5-7	NA[c]	0.931
DQDA-3270	23.3% ethyl acrylate	15	70-73	NA
DXQD-0457	14.6% ethyl acrylate	19.8	NA	NA
DQDA-3269	26.4% vinyl acetate	16.6	63-68	NA
DQDA-7268	29.5% vinyl acetate	ca. 300	59-61	NA
Zetafin 30	ethyl acrylate[b]	2.5	NA	0.928

[a] All obtained from Union Carbide except Zetafin 30 from Dow.

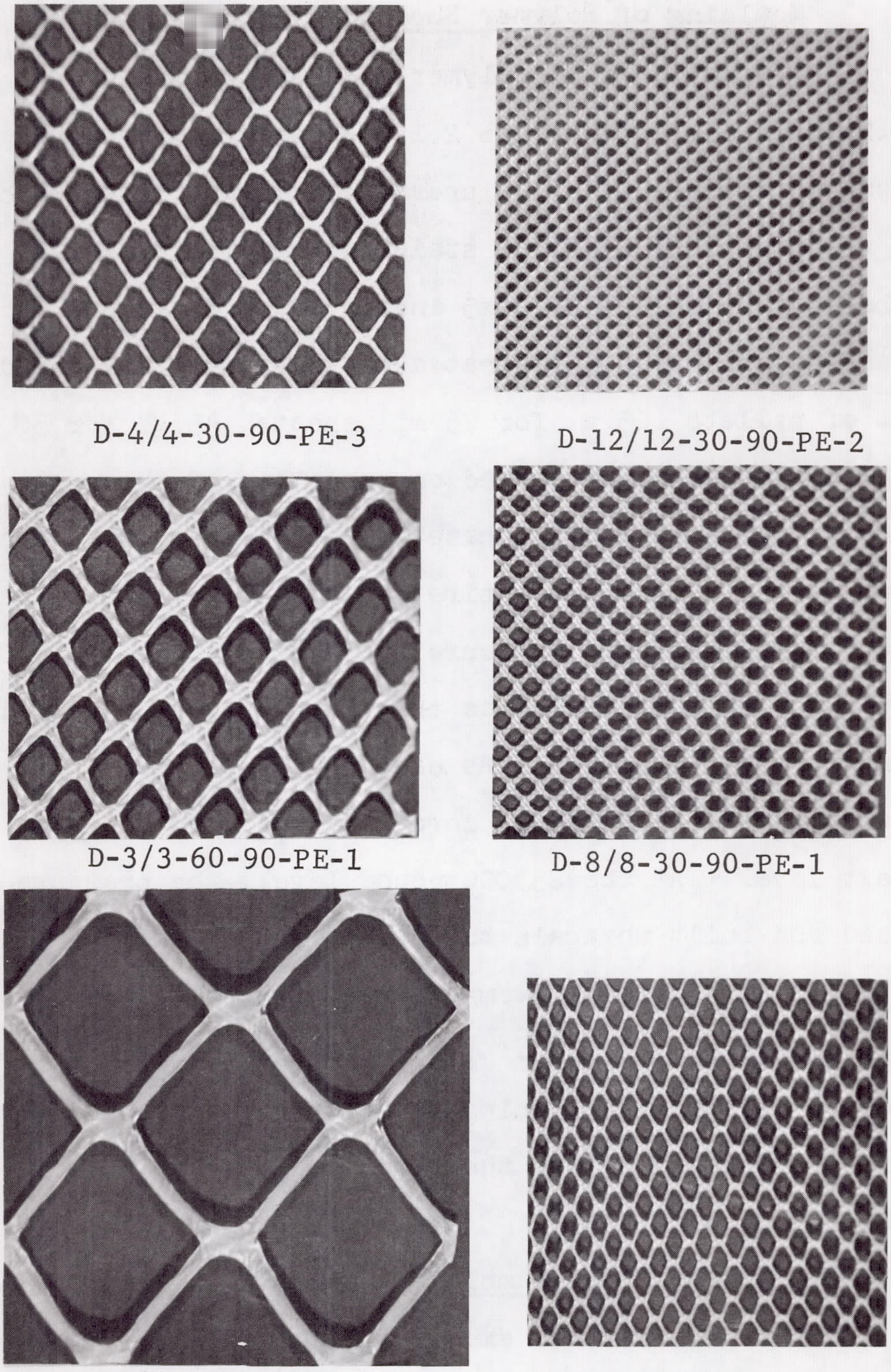
[b] Composition not available

[c] NA = Not Available

Except for Althons 15, 7010 and 7030, all of the polymer grades described in Table 2.1 were studied in the form of moulded sheets (see Section 2.2 for moulding procedures). Alathons 7010 and 7030 were employed in the form of 17-19 mil extruded sheets as supplied by DuPont; Alathon 15 as 52 mil tape. Marlex 5003 was used in the form of both moulded and extruded materia Extruded Marlex 5003 was supplied as 23 mil sheet by Phillips. Except for the thickness study (Section 4.1.2.6), all moulded sheets were employed in the thickness range of 55-60 mil. The extruded tape was 52 mil as indicated above, no attempt was made to compensate for this thickness difference and the Alathon 15 results have been compared directly with those of the slightly thicker moulded sheets.

The polyethylenes described in Table 2.2 were all extruded Vexar polyethylene mesh specimens supplied by DuPont and having varied thicknesses and mesh sizes. They were employed to study the restoration behavior of a mesh structure; high, medium and low density grades being included. These mesh grades are shown in Figure 2.1

The polyethylenes described in Table 2.3 are all copolymers containing more than 14% of a comonomer (either acrylate or acetate) that softens the polymer. They were employed to study the effect of copolymer composition on the memory effect. Except for DPDB-6169 and Zetafin 30, all of the other copolymers were experimental at the time of this work. These materials were moulded (Section 2.2) into 60 mil sheets. Moulded sheets of 120 mil thickness were supplied by Union Carbide.



D-4/4-30-90-PE-3

D-12/12-30-90-PE-2

D-3/3-60-90-PE-1

D-8/8-30-90-PE-1

D-1/1-100-90-PE-1

D-6/6-20-90-PE-3

FIGURE 2.1 Various Grades of Vexar Polyethylene Mesh

2.2 Moulding of Polymer Sheets

The moulding of polymer sheets (8x5 inches) of the polyethylenes listed in Table 2.1 was performed employing a Pasadena Hydraulics moulding press (containing internal heaters and a water cooling system), stainless steel plates (9x6 inches OD) and chases (9x6 inches OD, 8x5 inches ID). The upper and lower plattens of the press were heated to 300-350°F. and the desired amount of pellets (25 g. for 25 mil sheets, 45 g. for 50 mil and 100 g. for 150 mil) was placed on one plate of the mould and held within the confines of the chase. The second plate was placed over the material and the entire mould placed in the press and held under 1000 pounds. pressure for 5 minutes at the moulding temperature. The pressure was then increased to 23,000 lbs. in increments of 5000 pounds. As each 5000 pound level was reached, the pressure was released to zero lbs. and then built up to the next level. At the 23,000 pound level, the pressure was released and built up again to 23,0000 pounds and held for 5 minutes at the moulding temperature. The pressure was reduced to 1000 pounds at the end of this period and the system cooled to room temperature by running water through the plattens of the press. The sample was then removed from the mould and used for the memory studies.

2.3 Irradiation of Samples

All irradiations except the low dose-4.3 Mrads-irradiations were performed using a 1.5 Mev GS High Voltage Engineering Corp. Van de Graaff electron accelerator. Irradiations were performed in air by placing the samples on dry ice (to prevent heating) on trays which, in turn, sat on a moving belt that passed back and forth under the 13 inch scanned beam of the accelerator. Two Mrads were delivered to the surface of the polyethylene specimens with each pass under the beam. (The time interval between radiation passes varied from 20 seconds to 1-1/2 minutes depending on the total number of samples being irradiated at any one time.) The dose delivered to the sample increases with beam penetration through successive layers of the sample due to secondary ionization. This is taken into account and a uniform dose is delivered to all parts of our samples by turning the samples over after one-half of the desired total dose had been delivered.

The 4.3 Mrad samples were irradiated under nitrogen using the Co-60 gamma irradiator at Radiation Applications Inc.

The doses for the Co-60 irradiations were determined by ferrous sulfate dosimetry; those for electron accelerator irradiations by cellulose and polyvinyl chloride film dosimetry.

3.0 EXPERIMENTAL PROCEDURES

The experimental work on this project involved the determination of the restoration behavior of deformed polymer specimens. Specimens were heated, deformed by bending in half and folding to the desired angle of deformation while hot, and then cooled (quenched) to "freeze" them into their deformed shape. Restoration of the deformed specimens to their undeformed shapes was performed by reheating and the extent of restoration, the restoration forces and other restoration behaviors were observed.

3.1 Definitions of Experimental Terms and Conditions

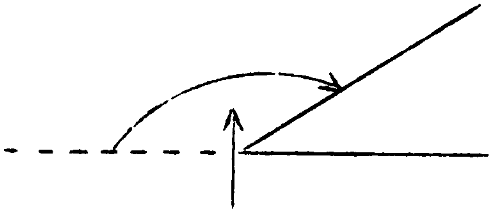
3.1.1 Deformation Conditions

The temperature at which the specimen is kept prior to its being deformed is defined as the deformation temperature. The time during which the specimen is kept at the deformation temperature is defined as the deformation time. The deformation temperature and deformation time are defined as the deformation conditions.

The development of transparency in irradiated polyethylene[14] represents a convenient point for classifying the type of deformation performed. When the test specimen is maintained at a deformation temperature above the T_m of the unirradiated polymer and becomes transparent, the process is called a Transparency deformation. This is also referred to as "T" deformation in this report. When the test specimen is maintained at deformation temperature below the polymer T_m, and remains opaque, the process is called a Non-Transparency deformation. This is also referred to as "NT" deformation.

3.1.2 Deformation Angle

When a test specimen is bent during the deformation process (after being subjected to the deformation conditions), it is changed in shape from a flat to an angular strip. The difference between the angle of the flat strip (zero degrees of deformation) and the deformed specimen is defined as the deformation angle.



Deformation Angle

3.1.3 Deformation Quench

After deformation the test specimen is cooled to lock in the memory. Cooling is accomplished by either immersion in cold water or maintaining in air at room temperature. A rapid cold water quench has been generally used in this work. This processing of "memory locking" is called the deformation quench.

3.1.4 Restoration Conditions

After deformation and quenching, the specimen is allowed to restore, i.e., exhibit its memory. This involves heating above ambient for some length of time. The temperature at which the sample is heated, after it has been deformed, is defined as the restoration temperature. The time the specimen is kept at the restoration temperature is defined as the restoration time. The restoration temperature and restoration time are defined as the restoration conditions.

3.1.5 Standard Conditions

In view of the large number of experimental parameters involved in studying the memory effect, it has been found convenient and desirable to define a set of standard conditions-one for T deformations and the other for NT-which have been employed in most experiments. When one parameter is under study, that is the only variable which is changed from these defined standard conditions. If more than one of these parameters are changed at one time, then this is specifically stated. The standard conditions are defined as follows:

(a) Polyethylene Grade: Grex 50-050
(b) Moulded Sheets
(c) Sample Dimensions: 1 cm. wide x 7 cm. long x 55-60 mil thick
(d) Radiation Dose: 61 Mrads
(e) Deformation: 80°C./1 hr. (NT)
140°C./to 5 min. (T)
(f) Deformation Angle: 180°
(g) Sharp Radius of Curvature
(h) Deformation Quench: 15°C./15 sec.
(i) Restoration Temp.: 140°C.
(j) Restoration Time: Variable

The reasons for these specific choices of NT and T standard conditions are indicated below:

(a) Grex 50-050 was chosen since it is of intermediate number average ($\overline{M}_n$) and weight average ($\overline{M}_w$) molecular weight and contains a small percentage of butene-1 as comonomer. The presence of butene-1 aids in stress crack resistance. The latter factor is of importance in this study where deformation is a prime factor. This polyethylene grade was thoroughly studied, while other grades were employed primarily for comparison, or to determine the effect of a specific polymer parameter.

(b) Moulded sheets were generally employed because of ease of preparation and availability of materials.

(c) To conveniently measure the degree of restoration and the restoring force, it was necessary to choose specimen dimensions that would give readily discernible values. Preliminary results indicated that test samples 7 cm. in length allowed deformation angle to be readily discernible; the 1 cm. width and 55-60 mil thickness allowed a mass of reasonable dimensions and size to be moved.

(d) A radiation dose of 61 Mrads was sufficient to allow the memory effect to be present and studied under T or NT deformation conditions, but was not so large as to cause cracking during experimentation, nor to (theoretically) greatly reduce the crystallinity.

(e) Deformation Conditions

(1) Non-Transparency (NT): 80°C./1 hr.

A deformation temperature of 80°C. was employed for NT deformations since it allowed only partial crystalline melting, but was sufficient to allow satisfactory deformations, to be performed. The time interval of one hour was sufficient to allow thermal equilibrium of the test specimens to be attained. Preliminary experiments indicated intermediate restoring forces after this deformation temperature.

(2) Transparency (T): 140°C./5 minutes

The 140°C. temperature is above the T_m of not only Grex 50-050 but of all the polyethylene grades employed in this study. Five minutes at this temperature was sufficient time for allowing transparency to occur.

(f) A deformation angle of 180° was employed since it allows for the most extreme type of deformation via bending alone.

(g) All of the deformed polyethylene specimens were bent in half so that essentially a 180° angle is obtained. The inner portions of the specimen were in a state of compression and the outer portions in a state of tension. All samples were bent sharply and considered to have a sharp radius of curvature (i.e., the diameter at the inside of the apex is equal to or less than the specimen's thickness - see Figure 3.1).

(h) The quenching or locking in of the memory of the deformed specimen was accomplished by cooling in a 15°C. water bath for 15 seconds. This allowed rapid cooling of the deformed specimens and was convenient.

(i) A restoration temperature of 140°C. allowed restoration to occur to completion regardless of the deformation conditions.

(j) The restoration time varied depending upon other parameters; however, it was always sufficient to allow an event to occur; i.e., partial restoration with no further determinable change, or attempted restoration with or without success. It varied from several seconds with restoration force measurements, to several weeks with degree of restoration measurements.

Standard conditions were employed for experiments in which one of the parameters (a to j) were under study. Variations from standard conditions were common, particularly in preliminary experiments.

3.2 Experimental Techniques

3.2.1 Deformation

Samples of dimensions 1 cm. width and 7 cm. length were placed in a silicone oil bath at the desired temperature and allowed to equilibrate. When the deformation was to transparency (T), the deformation time was generally 2-5 minutes at 140°C. When the deformation was to non-transparency (NT), the deformation time was one hour at the test temperature below T_m (40°C., 60°C., 80°C., or 100°C.). Samples were then removed and rapidly deformed while hot by folding to the desired angle and sharp radius of curvature. A pair of tongs or forceps was employed to perform the bending of the specimen; the deformation location was always 2 cm. from one end of the sample. After deformation, samples were quenched in cold water for 15 seconds at 15°C.

3.2.2 Degree of Restoration

Deformed specimens were placed in a silicone oil bath maintained at the desired temperature (140°C.). Restoration occurred and the decrease in the degree of deformation from an initial angle of deformation of 180° was observed visually over the desired time interval by laterally placing the specimen against the protractor. The latter was sometimes kept inside the liquid bath; sometimes the specimen was removed and placed against it. Removal was performed only when restoration was occurring slowly or was complete.

Some restoration tests were also performed in an air oven at 140°C. Some experiments were also performed with the restoration being performed laterally. Normal restoration behavior was observed to occur under these conditions. The density of the restoration liquid was not a factor in this measurement (or the restoring force measurement) as shown by the fact that the silicone oil ($d_{25} = 0.960$) could be replaced by 2-ethyl hexanol ($d_{25} = 0.833$) to yield identical results.

3.2.3 Restoring Force

The restoring force was determined by a method which involved moving or lifting of a mass (or, in gravity, lifting a weight) by the deformed specimen as it restored. The masses, consisting of flat lead strips, were (generally) of the same length and width as the upper part of the deformed specimen (i.e., 1 cm. x 5 cm.). They were attached and held in place on the upper length of the sample by means of a copper pin and clip. (This constitutes a mass-apex distance (i.e., the distance from the center of the mass to the apex of the sample) of 2.5 cm.) The sample was then placed on a metal stand and in turn held in place by a clamp located 1 cm. from the apex. The entire apparatus was placed in a silicone bath at the desired temperature and the restoration behavior observed. The experimental apparatus and procedures are shown in Figures 3.1 and 3.2, respectively.

Restoration was considered to have occurred when the sample lifted itself and the attached mass completely over the apex (i.e., $> 90^{\circ}$ angle), considering the apex as a relatively fixed point. Experiments were continued until the maximum mass that could be moved was obtained. The experimental points of maximum mass moved and minimum mass not moved were obtained to within at least 10% of each other for NT deformations. The values were less precise for T deformations (see Section 3.3). These points were then determined at least twice, and many

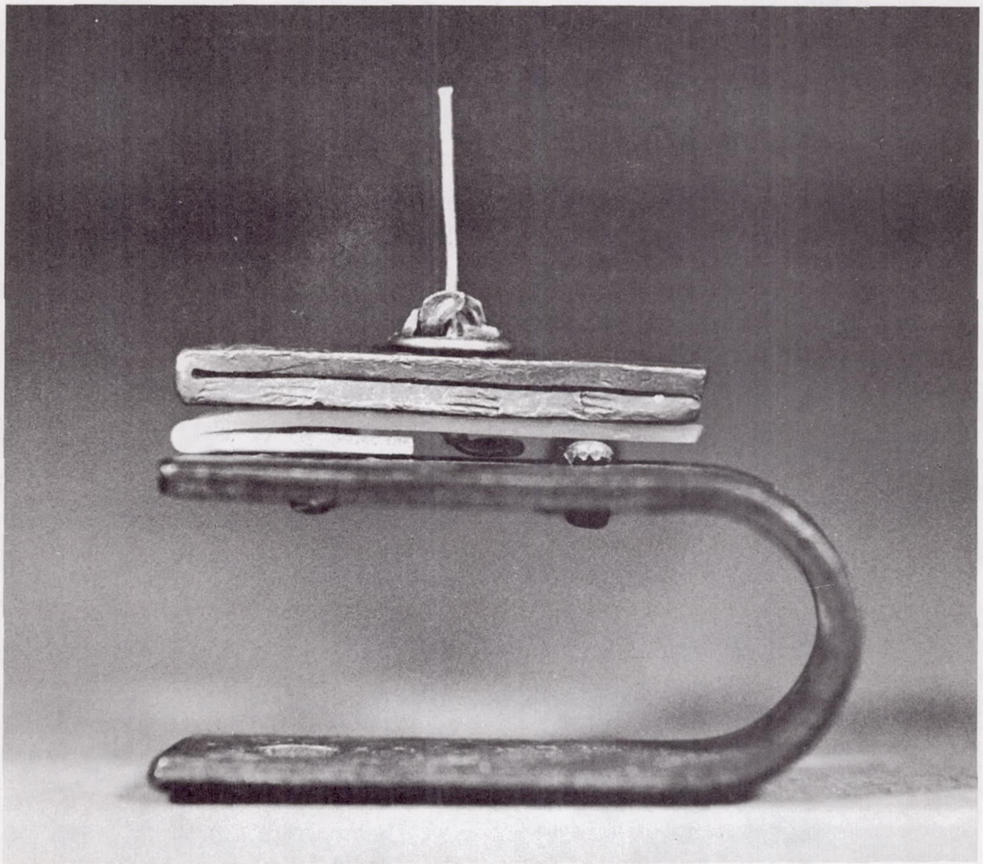


FIGURE 3.1 Experimental Setup (Holder, Deformed Sample, and Lead Weight) for Measurement of Restoring Force

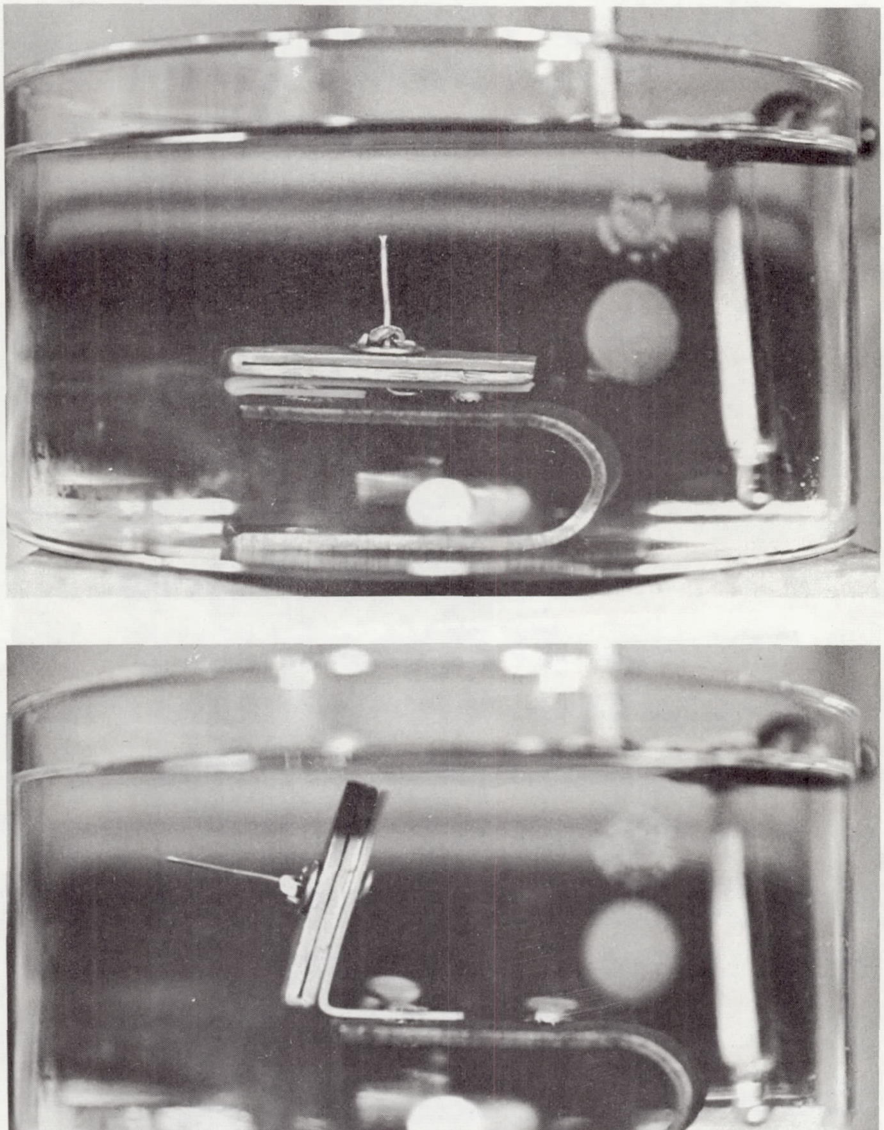


FIGURE 3.2 Experimental Procedure for Measurement of Restoring Force

experimental points were rechecked in triplicate and quadruplicate.

As the amount of applied mass is continually increased, the ability of the deformed specimen to move (or "lift") it decreases; eventually, a mass is applied on the specimen that is too great to be moved, and restoration does not occur. In practice, the average value between the maximum mass moved and the minimum mass not moved is obtained. The experimental value obtained is a maximum mass (gm.) moved by a specimen of specific dimensions. Since the distance (cm.) of the center of the mass to the apex (i.e., the mass-apex distance) is known, multiplication of this value by the maximum mass moved will give a moment value (gm.-cm.). In the report, restoring force data is given in both grams moved and in restoring moment (gm.-cm.). The latter data has been called restoring force. The calculated moments do not include the contribution due to the restoring sample lifting itself. This value is very small, the specimen portion itself weighing less than 0.5 gms.

3.2.4 Density

From time to time during the course of this investigation it became desirable to have a knowledge of the degree of crystallinity of the polymers being tested. As a rapid means of obtaining this measurement, the density of test specimens was obtained. (The limitations of various experimental methods employed for crystallinity studies have recently been discussed.[4])

The experimental method employed involved the suspension of pellets or sections of the polyethylene sheet in water, followed by titration with methanol until the polyethylene remained suspended (at a constant temperature of 25°C.) in the resulting solution for at least 30 minutes. The specific gravity of the solution was then determined by means of a Fischer-Davidson gravitometer.[15] The measurements of polymer density were reproducible to ± 0.003 gm./cc.

By determining the polymer density in this manner, it has been shown that appreciable changes in the apparent polyethylene density do not occur upon moulding sheets from pellets. The densities of all specimens tested remain the same to within ± 0.005. The effect of radiation has also been measured in this manner. Radiation has been reported to completely destroy polyethylene crystallinity after 500 Mrads.[6b] The highest dose tested in this study was 200 Mrads and this test apparently indicates negligible crystallinity lost at that dose; the result is in good agreement with the literature.[6] The results of the polymer density determinations on various specimens are listed in Table 3.1.

Table 3.1

Density[a] of Various Polyethylene Grades after Various Radiation Doses

Sample	Unirradiated		Irradiated			
	Pellets	Sheet	61 Mr.	104 Mr.	123 Mr.	245 Mr.
Alathon 14	0.911	0.918	-	0.919	-	-
Alathon 15	-	0.920	-	0.922	-	-
Alathon 7010	-	0.955	-	0.951	-	-
Alathon 7030	-	0.955	-	0.955	-	-
Alathon 7040	0.962	0.956	0.958	-	-	-
Grex 50-050	0.949	0.955	-	0.950	-	0.958
D 1/1-100-90-PE-1	-	-	-	-	-	0.922
D 8/8-30-90-PE-1	-	0.915	-	-	0.918	-
D 12/12-30-90-PE-2	-	0.921	-	-	0.928	0.931
D 6/6-20-90-PE-3	-	0.943	0.943	-	-	0.943
DPDB 6169	0.932	0.934	-	-	0.934	-
Zetafin 30	0.926	0.933	0.932	-	0.932	-

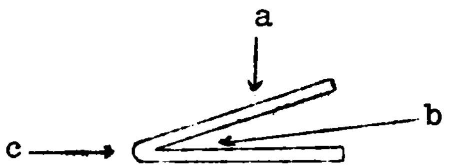
[a] Density = gm./cc.

This experimental approach was also employed to determine whether an appreciable density change occurred in T and NT deformed polyethylene. Test specimens from the portions of the deformed polyethylene in both tension and compression were placed in water and titrated with methanol until the pellet remained suspended. The experiments indicated no difference in density between the different regions of the deformed polyethylene. It is to be pointed out, however, that after T deformation, a lower density was observed relative to the original density. This indicates that recrystallization after T deformation is not as ordered as after initial moulding or after NT deformation. These results are indicated in Table 3.2.

Table 3.2
Density of Deformed Polyethylene

Polyethylene Grade:	Moulded Grex 50-050
Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil
Deformation:	80°C./1/2 hr. (NT); 150°C./3 min. (T)
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.

Deformation Type	Radiation Dose (Mrads)	Density (gm./cc.)			
		Undeformed Specimen	Unstressed Portion of Deformed Specimen[a]	Compressed Area of Deformed Specimen[b]	Tensed Area of Deformed Specimen[c]
NT	61	0.950	0.956	0.949	0.960
T	61	0.950	0.933	0.932	0.932
T	123	0.950	0.933	0.932	0.932



3.3 Limitations

3.3.1 Deviation from Rigid-Body Behavior

3.3.1.1 Angle Measurements

The measurement of the angle of deformation for NT restorations was relatively simple. However, when restoration was carried out such that transparency developed, the specimen was no longer rigid and the angle measurement was complicated. Thus, the buoyant force of the restoration bath fluid tended to impart a curvature to the restored specimen. Completeness of restoration was ascertained in such instances by removing the restored specimen from the bath and observing its angle of deformation. This value was always observed to be zero degrees, i.e., the sample was in its original flat shape once transparency occurred. As will become evident from the data in Section 4.0, T restoration results in essentially complete restoration. (Throughout this report, the terms "essentially complete restoration" and "complete restoration" are used interchangeably to indicate restoration which is complete to within ca. 1° of deformation angle.)

3.3.1.2 Restoring Force Measurements

The experimental measurement of restoring force, as performed in this study, involves the movement of a mass by a lever arm about a "hinge" (i.e., the deformed portion of the polyethylene). When the maximum mass that can be moved by the deformed specimen has been determined, the restoring moment is calculated by multiplying this value by the mass-apex distance (i.e., the distance from the bend to the center of the mass). Certain assumptions are implied in this type of measurement. These are that (1) the deformed section of the bend behaves as a true fixed hinge, (2) the material behaves in a manner identical to that of a rigid lever arm, and (3) the restoration media does not affect the restoration behavior. In actuality, the first two assumptions are not completely correct. Indeed, it was seen in the previous Section (3.3.1.1) that the restoration media can impart a curvature to the polyethylene specimen after it has become transparent, despite a thickness of 55-60 mil. High density polyethylene, while rigid in thick (ca. 50 mil) pieces at ambient temperatures, is very flexible in thin (ca. 10 mil) slices. Low density polyethylene is flexible even in thick 50 mil strips. Furthermore, regardless of either thickness or density, polyethylene becomes less rigid as it is heated and approaches its T_m. Irradiated polyethylene is a flexible elastomer above its T_m. This flexibility manifests itself in two ways affecting the lever arm. The lever arm is not always rigid but is often "floppy" in nature, and samples sometimes showed an increase in radius of curvature upon restoration.

Under standard conditions, two types of behavior upon restoration occurred with masses attached to the samples. Specimens deformed under NT conditions restored by lifting straight up from the apex, while those deformed under T conditions restored by an apparent rolling and lifting action. This latter type of restoration was accompanied by an increase in the radius of curvature at the apex. The lack of rigidity in the lever arm was observed under the following three sets of conditions:

(a) In high density NT deformed specimens, when the mass on the sample was considerably greater than the maximum which could be lifted, the load caused a bowing of the lever arm. /‾Since these conditions did not yield any desired experimental data, they were not of importance in this study._7 Significant data was obtained only when the mass was in the vicinity of the maximum and the lever arm remained rigid.

(b) In low density NT deformed specimens, when the load was in the approximate vicinity of the maximum, bowing generally occurred.

(c) A radius of curvature increase at the apex was observed upon restoration of all T deformed specimens, regardless of composition or density. This occurred as a result of T deformation requiring transparency for restoration, and was prevalent when the mass on the specimen was in the vicinity of the maximum that could be moved. (See Figure 3.3).

A critical evaluation of the data, which is given in Section 3.3.2, indicates that despite the lack of rigid behavior under some test conditions, the data is sufficiently accurate to ± 10-15%.

It is of importance to consider the contribution to the total work performed by the restoring specimen in overcoming the viscous drag of the bath liquid on the moving specimen leg and affixed weights. We have performed calculations in order to determine the magnitude of this work, based on the use of Stokes law[16] for the viscous or laminar flow of spherical

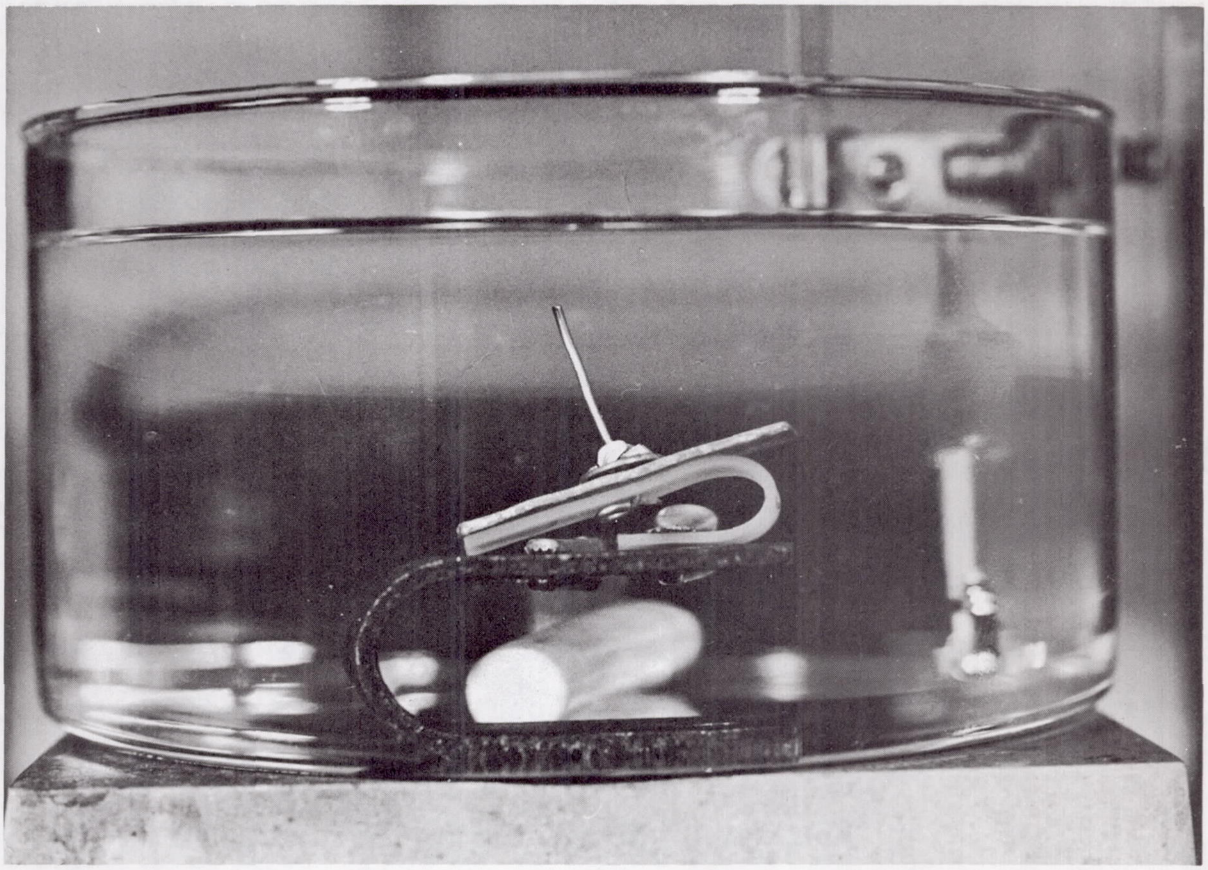


FIGURE 3.3 Radius of Curvature Change During Measurement of Restoring Force

particles:

$$F_d = 3\pi Duv$$

where F_d = resistance offered by the liquid

D = diameter of spherical body

u = viscosity of liquid

v = velocity of body relative to liquid

It should be noted that Stokes law holds for spherical particles; since the restoring specimen was a rectangular parallelopiped and not a sphere, an approximation had to be made. Several ways of expressing D are possible. One could express D as the

1. diameter of a sphere of surface area equal to that of the top portion of the specimen rectangular parallelopiped,
2. diameter of a sphere of equivalent volume,
3. length of the top portion of the specimen.

Calculations were performed using all three approximations. The moment due to F_d was calculated for all three approximations to be approximately 100 dyne-cm. This is quite small and is negligible compared to the work involved in the moving of the affixed weights. Because of the small contribution of F_d to the total restoration work, more refined calculations of F_d were not performed.

3.3.2 Precision and Accuracy of Restoring Force Measurements

(a) NT Deformation

The precision of the restoring forces for NT deformation was ascertained by checking the results in a large number of identical experiments. Under standard NT conditions, the restoring force for Grex 50-050 varied from 290 to 335 gm.-cm., with the average being about 315 gm.-cm. (ca. ±8%).

Other conditions of testing after NT deformation were also investigated. Additional factors involved in this testing are

(1) the center of the mass-apex distance,
(2) relative dimensions of the mass and sample, and
(3) relative distance of the edge of the mass from the apex.

All of the experiments described in this report involve a mass-apex distance of 1.5-2.5 cm. (mainly 2.5 cm.), a mass and a specimen of essentially the same dimensions, and the coincidence of the edge of the mass and the apex during testing. These, however, are arbitrary conditions chosen for convenience. It was of importance to determine the effect, if any, of changing these parameters on the restoring moment value obtained.

Table 3.3 shows the results of tests in which these parameters were changed. The mass center-apex distance was varied from 2.5 to 5.0 cm., the mass length was varied relative to the specimen's size, and the mass edge-apex distance was varied from 0 cm. (coincident) to 4 cm. All other testing conditions were standard. It is seen that restoring force values vary somewhat under the variety of conditions employed. The average value is 300 ± 20 gm.-cm. (i.e., 6-7% precision). It is concluded, therefore, that the moment law is validly applied here, and that the values obtained for restoring force are accurate to ca. ±10%. A similar study with the less rigid Alathon 15 yielded similar results as regards the validity of the moment law and the precision of the restoring force measurements.

Table 3.3

Precision of Mass Movement Experiments for NT Deformation

Polyethylene Grade: Moulded Grex 50-050
Sample width: 1 cm.
Sample thickness: 55-60 mil
Radiation Dose: 61 Mrads
Deformation: 80°C./1 hr. (NT)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Temp.: 140°

Mass placement[a]	Sample length (cm.)	Sample top length (cm.)	Mass length (cm.)	Mass-Apex distance[b] (cm.)	Mass Edge-Apex distance[c] (cm.)	Restoring Mass (gm.)	Force Moment (gm.-cm.)
A	7	5	5	2.5	0	125	315
A	7	5	5	3.6	0	75	270
A	9	7	7	3.5	0	85	300
A	10	8	8	4	0	75	300
A	12	10	5	5	0	55	275
B	9	7	3	3.5	2	100	350
B	12	10	5	5	4	55	275

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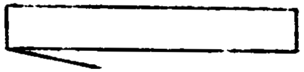
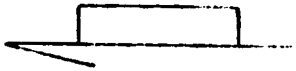
[a]



A



B

[b] Distance from center of mass to apex of specimen

[c] Distance from nearest edge of mass to apex of specimen

(b) T Deformation

A measure of the precision of the T deformation technique for Grex 50-050 was obtained employing mass-apex distances of 1.55-1.60 cm. and 5.0 cm. (In the latter case, the masses did not extend across the entire length of the specimen, but a mass edge-apex distance of 4.0 cm. was present.) The results, shown in Table 3.4 indicate the moments to be 10.3 ± 0.7 gm.-cm. (7% precision), and 7.6 ± 0.7 gm.-cm. (9% precision) respectively for the two mass-apex distances. In both cases, despite the radius of curvature change, reproducible results to ca. ±10% are obtained. The fact that the restoring moments vary by ca. 2.5% for the two mass-apex distances of 1.6 and 5.0 cm. may mean that the moment law is not as valid for T measurements as for NT due to the more flexible nature of the polymer under the former conditions. The discrepancy may also be due, simply, to the fact that the measurement of the smaller T restoring moments is less accurately measured.

Table 3.4

Accuracy of Mass Movement Experiments for T Deformation

Polyethylene Grade:	Moulded Grex 50-050
Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil for
Mass Apex Distance:	1.6 cm.
Sample Dimensions:	1 cm. x 10 cm. x 55-60 mil for
Mass Apex Distance:	5.0 cm.
Radiation Dose:	61 Mrads
Deformation:	150°C./3 min. (T)
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Restoration Temp.:	140°C.

Mass-Apex Distance: 1.6 cm.		Mass-Apex Distance: 5.0 cm.	
Mass Employed (gm.)	Restoration	Mass Employed (gm.)	Restoration
8.22	No	3.11	No
6.14	No	2.11	No
4.00	Yes	1.65	Yes
5.27	Yes	1.86	No
5.89	Yes	1.86	No
6.03	Yes	1.65	No
6.11	Yes	1.51	No
6.15	Yes	1.51	No
6.21	Yes	1.25	Yes
6.31	No	1.51	No
6.31	Yes	1.51	Yes
6.48	No	1.86	No
6.48	Yes	1.86	No
6.87	Yes		
6.87	Yes		

4.0 EXPERIMENTAL RESULTS

4.1 Polyethylene Homopolymer and Polyethylene-Butene Polymer

4.1.1 Degree of Restoration

The degree of restoration of irradiated polyethylene was studied as a function of the various parameters discussed in Section 3.1. Standard conditions were employed to obtain this data, unless otherwise noted. The results are discussed below.

4.1.1.1 Deformation Conditions

The effect of the deformation conditions on the degree of restoration was studied by varying the deformation temperature over 40-140°C. It was observed that, regardless of the temperature at which deformation was performed, the degree of restoration was always complete if the restoration temperature was above the T_m of the unirradiated polymer. Neither the deformation temperature nor the deformation time affect the degree of restoration. However, the total restoration behavior is affected by the deformation temperature. The lower the deformation temperature, the more rapidly does restoration begin; as the deformation temperature is increased (from 40°C.), the onset of restoration is delayed. When deformation is performed under transparency conditions, the time interval between immersion in the hot environment and the beginning of restoration is greatest. Regardless of this effect, controlled by the deformation conditions, restoration is always essentially complete under otherwise standard conditions. These results are briefly shown in Table 4.1.

Table 4.1

Deformation Temperature Effect on Degree of Restoration

Polyethylene Grade: Moulded Grex 50-050
Sample Dimensions: 1 cm. x 7 cm. x 55-60 mil
Radiation Dose: 61 Mrads
Deformation: 1 hour
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Temp.: 140°
Restoration Time: to 1 hour

Deformation Temperature (°C.)	Restoration	Comments
40	Complete	Begins immediately (< 10 seconds)
80	Complete	Begins later than 40°C. sample
140	Complete	Begins late (2-3 min.); shortly before transparency

Unirradiated polyethylene can be deformed at temperatures below its T_m (i.e., 40-120°C.); upon being placed in a hot environment at 140°C., these specimens begin to restore. However, restoration is incomplete, and melting of test specimens occurs as they approach 140°C. (i.e., the polymer T_m).

4.1.1.2 Restoration Conditions

(a) Temperature of Restoration

The effect of restoration conditions was studied by performing tests over the 40-140°C. temperature range. The restoration time was allowed to be long enough so that thermal equilibrium between the sample and environment was established, and, therefore, it did not become a factor.

The restoration temperature was found to be of profound importance in controlling the degree of restoration of NT deformed polyethylene. Restoration begins to occur over the entire testing temperature range. However, the degree of completion is greater as the restoration temperature is increased. For restoration to be complete, the environmental restoration temperature must be above the T_m of the unirradiated polymer. Table 4.2 and Figure 4.1 show the effect of the restoration temperature on the degree of restoration of NT deformed, high density Grex 50-050 polyethylene. It is seen that complete restoration occurs at 140°C. but not at 120°C. or lower. Restoration in all these cases begins almost immediately. It proceeds to different extents controlled by the deformation temperature.

When Alathon 15, low density polyethylene, is tested in a similar manner, it is observed that restoration is essentially complete at 120°C., but not at 90°C. The T_m of this low density polyethylene is 105°C.

T deformation (140°C.) was studied in a similar manner with Grex 50-050 (Table 4.3). The restoration temperatures employed were 40-140°C. It was observed that restoration did not occur at the lower restoration temperatures. As the restoration temperature is raised, no change occurred until the T_m was approached. The onset of restoration occurred slightly below the T_m. Restoration was complete only above the polymer T_m. When restoration did occur, it did not begin immediately; the approaching of thermal equilibrium with the environment was required. It was only at temperatures greater than the T_m that transparency occurred and restoration was complete.

Unirradiated Grex 50-050 polyethylene was also tested in a similar fashion to determine the restoration temperature effect on the degree of completion of restoration. Standard NT deformation conditions were employed to prevent complete melting

Table 4.2

Restoration Temperature Effect on Degree of Restoration

Polyethylene Grade: Moulded Grex 50-050
Sample Dimensions: 1 cm. x 7 cm. x 55-60 mil
Radiation Dose: 61 Mrads
Deformation: 80°C./1 hr. (NT)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.

Restoration Temperature (°C.)	Degree of Restoration	Comments
40	partial	restoration to 90° angle in less than 2 minutes; same after hours[a]
60	partial	restoration to 45-50° angle in less than 2 minutes; same after hours
80	partial	restoration to 45-50° angle in less than 2 minutes; same after hours[b]
120	partial	restoration to 25-30° angle in less than 2 minutes; same after hours[c]
140	complete	restoration in less than 5 minutes; essentially complete at transparency[d]

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[a] unirradiated specimen restores to ca. 105° angle

[b] unirradiated specimen restores to ca. 40° angle

[c] unirradiated specimen restores to ca. 20° angle

[d] unirradiated specimen melts.

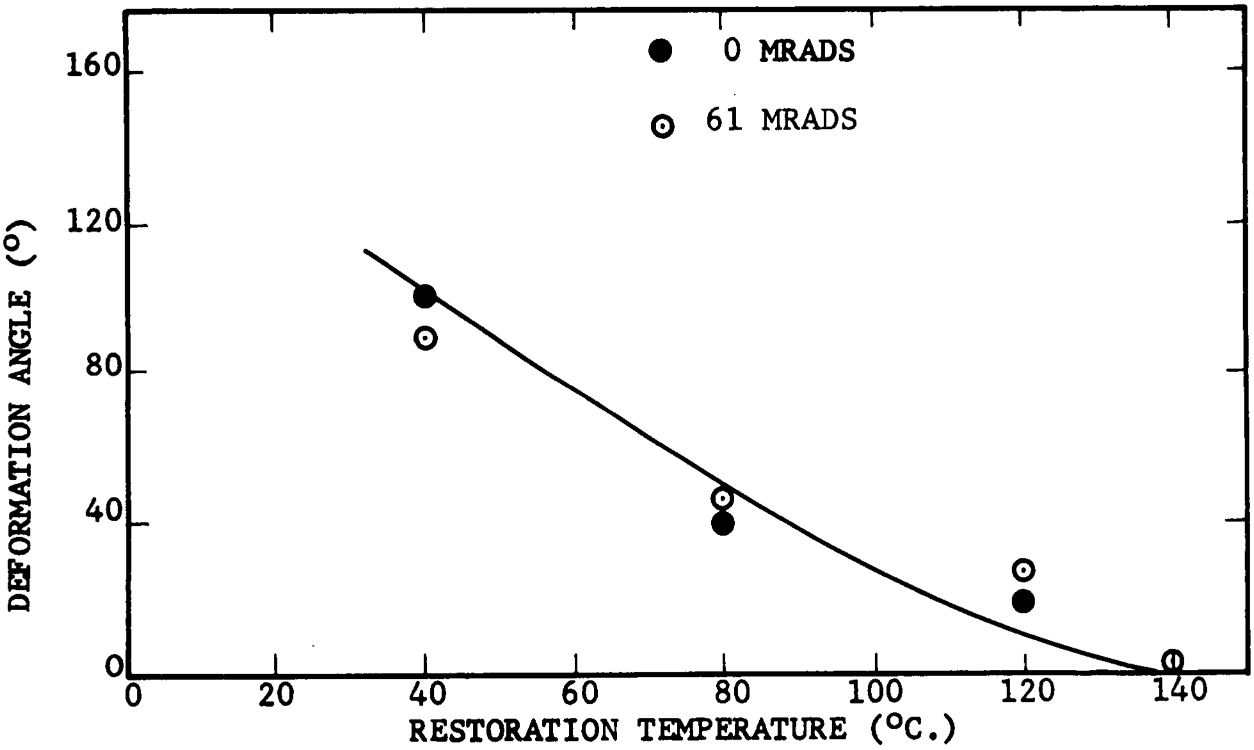

FIGURE 4.1 Restoration Temperature Effect on Degree of Restoration of Grex 50-050 (NT)

Table 4.3

Restoration Temperature Effect on Degree of Restoration

Polyethylene Grade:	Moulded Grex 50-050
Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil
Radiation Dose:	61 Mrads
Deformation:	140°C./1 hr. (T)
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Restoration Time:	1 - 1½ hours

Restoration Temperature (°C.)	Degree of Restoration	Comments
40	none	no change in deformation angle
80	none	no change in deformation angle
120	partial	restoration to about 110° angle in 5 minutes; no further change in hrs.
140	essentially complete	restoration in less than 5 minutes

during deformation. It was observed that, as with irradiated polyethylene, the degree of restoration is dependent upon the restoration temperature. The restoration temperature dependency on the degree of restoration is essentially identical for irradiated and unirradiated specimens (see Figure 4.1).

(b) Restoration Medium

Although the degree of restoration is independent of the deformation conditions, it is highly dependent on the temperature of restoration. The question naturally arises as to whether the environmental media during restoration testing is a factor in the results obtained. The nature of the liquid employed was shown to be immaterial, at least throughout the density range studied, by substituting silicone oil ($d_{25} = 0.960$) for 2-ethyl hexanol ($d_{25} = 0.833$) and obtaining identical results.

Identical experiments were also performed by heating deformed samples in an oven at the same temperature of the liquid bath (140°C.). This approach had the disadvantage of requiring a longer time for heating (due to slower heat transfer) and for restoration to occur. It had the advantage of more closely simulating the practical end use method of heating the specimen in space. It was observed that restoration was always essentially complete over a matter of minutes.

Differences between T and NT deformed specimens were apparent on the basis of the time required for restoration to begin. NT deformed specimens (standard conditions) of Grex 50-050 began to restore immediately in the 140°C. oven, were about 80% complete in 3-5 minutes while remaining non-transparent and were essentially complete in 10-15 minutes, at which time transparency occurred. The specimen arm remained rigid during the initial

80% return since little or no crystalline melting occurred during that interval. T deformed specimens (standard conditions) did not begin to restore for about 5 minutes (the time required for the specimen to reach equilibrium with its environment). Restoration then occurred over another 5-10 minute interval, after which it was essentially complete. The specimen arm did not remain completely rigid during restoration. The differences in behavior imparted to the polyethylene under various deformation conditions became apparent, therefore, under either the liquid bath or air oven methods of inducing restoration. It is notable that NT deformed specimens are over 80% restored by the time T deformed specimens begin to restore.

In actual practice for space erectable structure applications, restoration would be brought about by the use of a degradable coating that would initially absorb heat to enable restoration to occur, and then would itself degrade. Much research has been, and is presently being performed on potential coatings for this purpose in the space environment. Studies into methods of controlling temperatures on objects in space[17-19] and on the degradation of polymers in space[19-21] indicate substantial recent progress in this area.

4.1.1.3 Radiation Dose

The effect of radiation dose on the degree of restoration of Grex 50-050 was studied over the 0-184 Mrad range. The results, given in Table 4.4 and Figure 4.2, indicate that the radiation dose does not influence the degree of restoration for a polyethylene possessing a $\overline{M}_w$ at least 70,000. Regardless of the radiation dose, at or above 12 Mrads, resto-

Table 4.4

Radiation Dose Effect on Degree of Restoration

Polyethylene Grade: Moulded Grex 50-050
Sample Dimensions: 1 cm. x 7 cm. x 55-60 mil
Deformation: 80°C./1 hr. (NT); 140°C./1 hr. (T)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Time: 1-3 days

Radiation Dose (Mrads)	Restoration Temperature (°C.) 40	80	120	140
	Deformation Angle (°)			
80°C. DEFORMATION TEMPERATURE (NT)				
0	105	40	20	melts
12	85	40	25	complete
61	90	45	25	complete
123	115	30	20	complete
184	90	30	20	complete
140°C. DEFORMATION TEMPERATURE (T)				
12	180	180	ca. 60	complete
61	180	180	ca. 20	complete
123	180	180	ca. 10	complete
184	180	180	ca. 10	complete

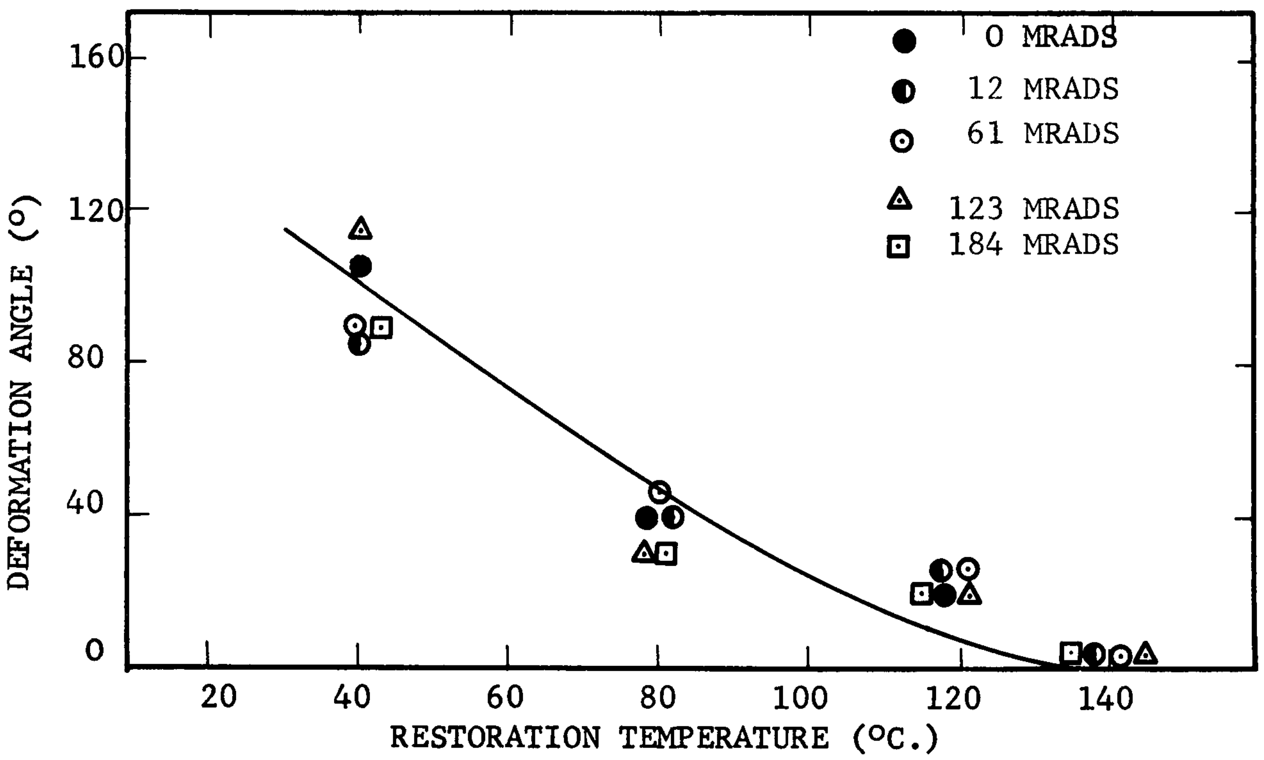

FIGURE 4.2 Radiation Dose Effect on Degree of Restoration of Grex 50-050 at 80°C. Deformation Temperature

ration is always essentially complete at 140°C. for both T and NT deformations. However, when the polyethylene molecular weight was 2500, even 61 Mrads was insufficient to allow restoration to occur. This is discussed in Section 4.1.1.5. Unirradiated controls, tested under restoration temperatures below the T_m, behaved similar to irradiated specimens.

The effect of lower radiation doses ($<$ 12 Mrads) on the degree of restoration was studied at one experimental point-4.3 Mrads. Grex 50-050, deformed and restored at 140°C. under standard conditions, did not restore completely. The test specimens restored partially after 1 minute (transparency occurred on restoration) but (a) the hump imparted during the deformation process remained, and (b) marks on the polyethylene due to the pressure of the forceps employed during the deformation process to hold the sample did not disappear. (At 12 Mrads and above the development of transparency always eliminates the hump and any forceps indentations that may be present.) Results were exactly the same after 30 minutes, long after transparency developed. The failure of the hump and forceps marks to disappear indicates that a permanent deformation of significant proportion has been imparted to the polyethylene. Sufficient crosslinking for the development of true elastomeric behavior is absent. Similar observations regarding incomplete restoration were made as a result of stretching 4.3 Mrad Grex 50-050 and Marlex 6002. Restoration was incomplete.

It may be concluded that 4.3 Mrads are sufficient to allow partial restoration, but insufficient to allow complete restoration. Twelve Mrad polyethylene does allow restoration to be complete under identical conditions. (Since 12 Mrads yield over 50% gel (i.e., insoluble fraction) while 4.3 Mrads give about 25% gel,[8] the critical gel region for allowing essentially complete restoration to occur is within this range.)

4.1.1.4 Crystallinity

The effect of polyethylene crystallinity on the degree of restoration was observed by studying the memory of polyethylenes of varying density and crystalline melting point (T_m)under standard NT deformation conditions. Under these conditions, only partial crystalline melting occurs prior to deformation and the nature of the restoration process can be expected to depend primarily on the initial polymer crystallinity.

The data, shown in Table 4.5 and Figure 4.3, indicates that the degree of restoration is very significantly influenced by the polymer density and crystalline melting point both of which are a measure of the polymer crystallinity. It is seen that the restoration is complete if the restoration temperature is above the T_m of the unirradiated polymer. The restoration temperature is lower for low density than for high density polyethylene. At restoration temperatures below the normal T_m, restoration is only partial. Thus, low density polyethylenes restore to a greater extent than high density grades at a specific temperature. It is of interest to note that the medium density (0.939) Hi-Fax 1901 requires the same restoration temperature as the high density (0.96) polyethylenes due to its T_m being of the same order as the latter.

Table 4.5

Density Effect on the Degree of Restoration

Moulded
Sample Dimensions: 1 cm. x 7 cm. x 55-60 mil
Radiation Dose: 61 Mrads
Deformation: 80°C./1 hr. (NT)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Temp.: 140°C.
Restoration Time: to 24 hours

Polymer Grade	Density (gm./cc.)	T_m (°C.)	Restoration Temperature (°C.)			
			40	80	120	140
			Deformation Angle (°)			
Alathon 14	0.914	108	70	15	0	0
Alathon 15	0.917	111	70	15	0	0
Hi-Fax 1901	0.939	129-131	100	45	35	0
Grex 50-050	0.950	131-132	95	45	25	0
Marlex 5003	0.950	124	115	30	20	0
Alathon 7040	0.957	132-135	120	45	20-25	0
Alathon 7511	0.960	132-135	115	40	20	0
Marlex 6002	0.960	127	110	40	25-30	0

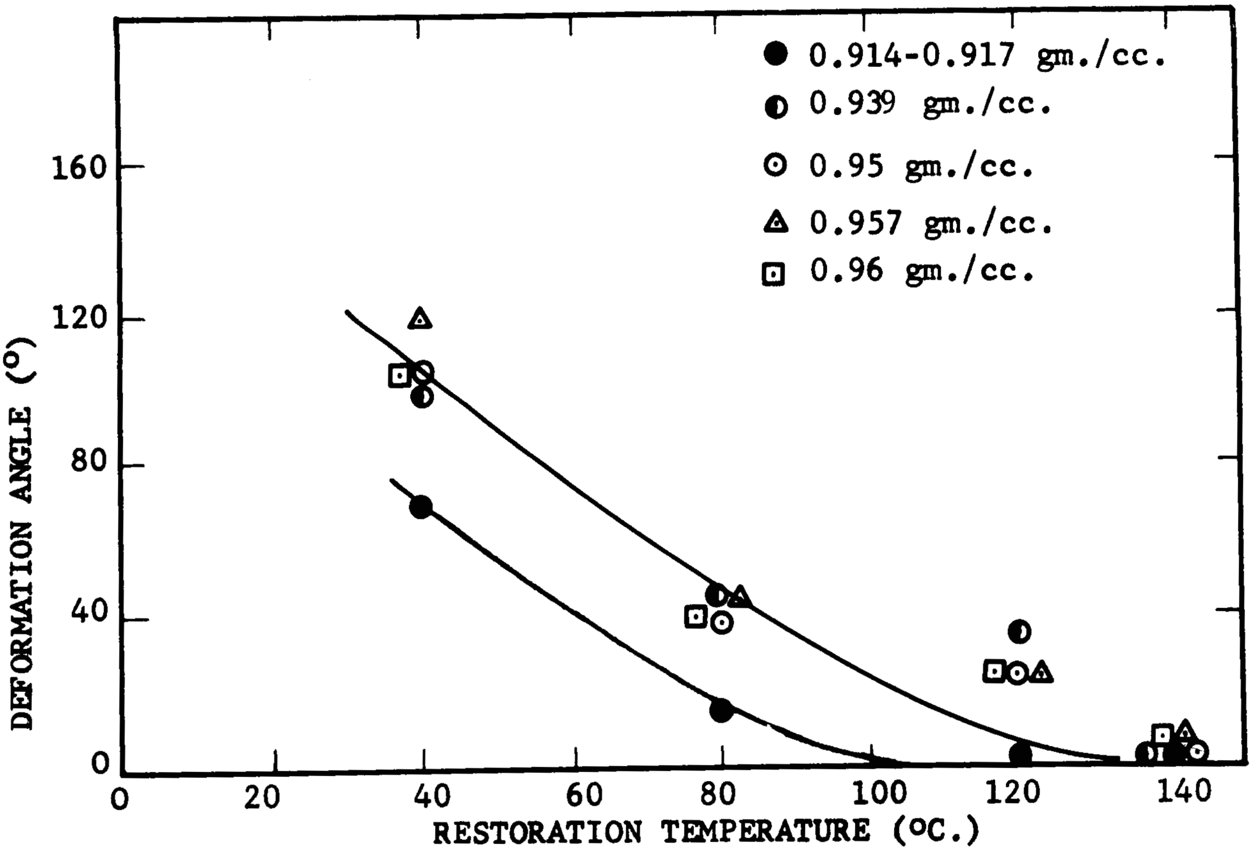

FIGURE 4.3 Density Effect on the Degree of Restoration

4.1.1.5 Initial Molecular Weight

The effect of polyethylene molecular weight on the degree of restoration was studied by testing many polyethylene grades (of different molecular weight) employing standard T deformation conditions. In this manner, complete crystalline melting occurs prior to deformation and complete crystalline melting must occur a second time prior to restoration. This implies that molecular weight will be the predominant factor in the degree of restoration. The polymer density can be expected to be a minor factor in such a test.

It was observed that restoration was always essentially complete for polyethylenes of $\overline{M}_w$ = 70,000 or above. The restoration temperature was, naturally, above the normal polymer T_m (140°C.). The degree of restoration is, therefore, independent of polymer molecular weight in this range. The next lowest polyethylene molecular weight tested was 2500 (Epolene E-10). This polymer could not be deformed satisfactorily as it melted. Presumably, when the molecular weight is this low, even a radiation dose of 61 Mrads is insufficient to give an extensive gel network.[6]

Employing lower restoration temperatures (40-120°C.), the nature of the restoration process for all these polymer grades (except that of 2500 molecular weight) was observed to be similar to T deformed Grex 50-050. Restoration did not begin to occur unless the restoration temperature approached the vicinity of the T_m. The results of this work are outlined in Table 4.6.

Table 4.6

Molecular Weight Effect on the Degree of Restoration

Moulded
Sample Dimensions: 1 cm. x 7 cm. x 55-60 mil
Radiation Dose: 61 Mrads
Deformation: 140°C./5 min. (T)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Temp.: 140°C.
Restoration Time: to 17 hours

Polymer Grade	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	Restoration Temp. (°C.)			
			40	80	120	140
			Deformation Angle (°)			
Epolene E-10	2.5	-	-	-	-	melts
Grex 50-050	70-80	6-7	180	180	135	0
Alathon 7040	88	11-12	180	180	180	0
Alathon 7511	150-175	15-20	180	180	180	0
Marlex 6002	171	14	180	180	180	0
Marlex 5003	188	11	180	180	180	0
Alathon 15	500	15-20	180	180	0	0
Alathon 14	800-1000	22-26	180	180	0	0
Hi-Fax 1901	> 2000	-	180	180	120-125	0

4.1.1.6 Low Temperature Ageing or Storage

A characteristic of irradiated NT deformed polyethylene is its ability to "creep" or partially restore on storage at ambient temperatures (T deformed polyethylene does not exhibit this phenomenon.) The lower the deformation temperature, the more pronounced this effect. For example, with a deformation temperature of 35°C. for Grex 50-050, 70% restoration can occur in four days; the degree of restoration at ambient temperature after that time for ca. 70°C. deformation is approximately 50%. The data in Table 4.7 and Figure 4.4 indicate the magnitude of this effect for various polymers under various deformation conditions. The effect is most pronounced initially and then tapers off. Increased radiation dose had no effect. Grex 50-050 irradiated to 123 Mrads and Alathon 15 irradiated to 123-245 Mrads

Table 4.7

Restoration at Ambient Temperature

Moulded	
Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil
Radiation Dose:	61 Mrads
Deformation:	1 hour
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Restoration Temp.:	Ambient

Polymer Grade	Deformation Temp. (°C.)	Restoration Time	Deformation Angle (°)
Grex 50-050	35	Initial	180
		1 min.	130
		4 days	60
	67	Initial	180
		1 min.	170
		4 days	110
		7 days	105
Alathon 15	35	Initial	180
		1 min.	50
		4 days	20
	67	Initial	180
		1 min.	165
		4 days	125
		7 days	125
Marlex 5003	74	Initial	180
		1 min.	150
		4 days	100
		9 days	95
Marlex 6002	74	Initial	180
		1 min.	140
		4 days	90

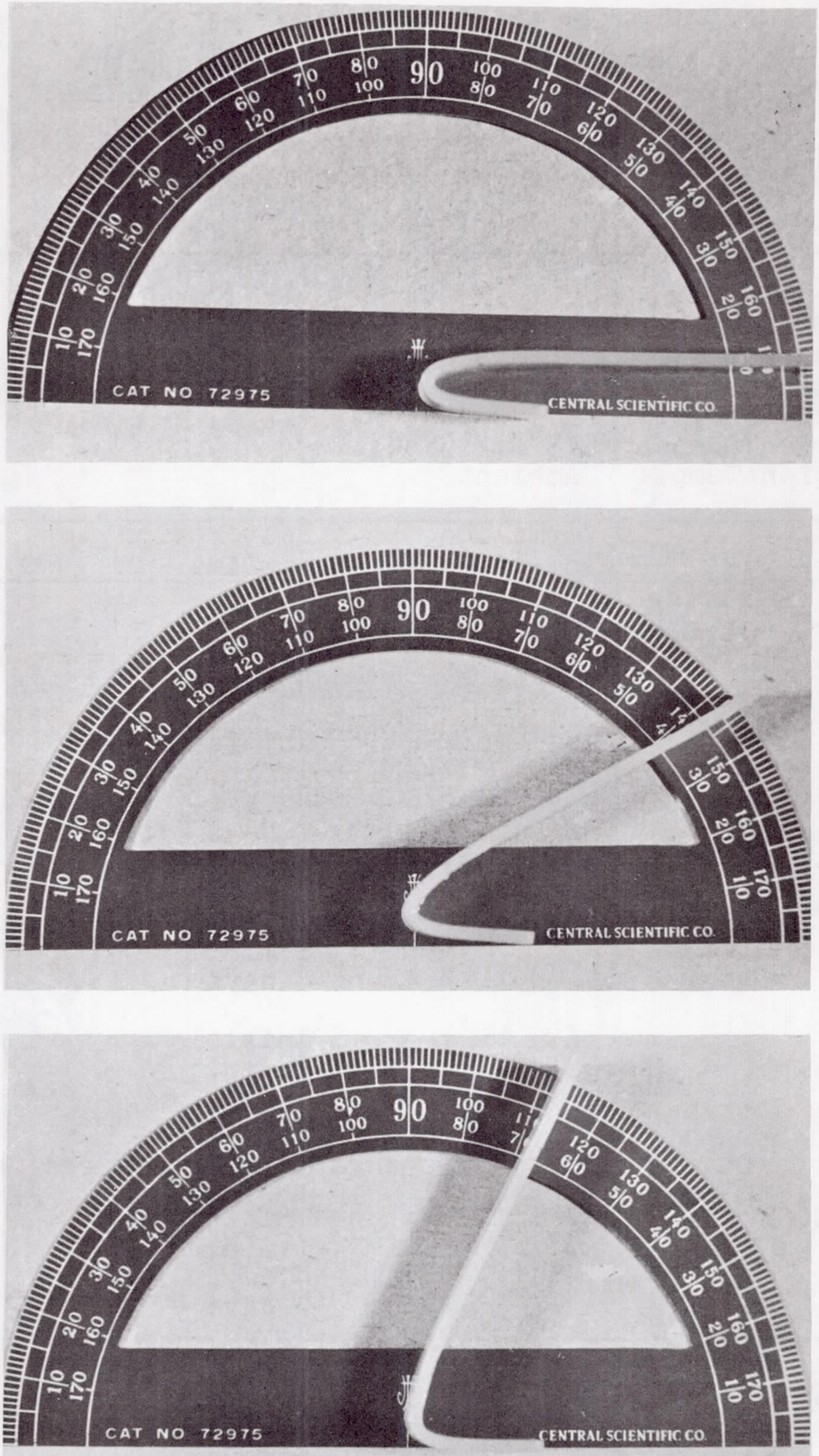

FIGURE 4.4 Restoration at Ambient Temperatures of NT Deformed 61 Mrad Grex 50-050
The time span between (a) and (c) is 5 minutes.

behaved similar to the 61 Mrad samples described in Table 4.7.

This phenomenon was of importance when long term ageing is considered. (For restoring force measurements, rapid experimentation minimized or eliminated the problem.) To this end, low temperature storage was investigated. This was performed experimentally by deforming specimens under standard conditions, followed by storage in a freezer at -10 to -15°C., and in an acetone-dry ice environment (-78°C.). It was observed that "creep" could either be retarded or prevented from occurring when stored at these temperatures. The greatest restoration occurred during the interval between the completion of deformation and the equilibration of the test specimen with the cold environment. These results are shown in Table 4.8 The use of low temperature storage as a means of reducing or eliminating creep (i.e., restoration) of aged, deformed specimens is a promising technique.

Table 4.8

Low Temperature Storage Effect on Degree of Restoration

Moulded
Sample Dimensions: 1 cm. x 7 cm. x 55-60 mil
Radiation Dose: 61 Mrads
Deformation: 72°C./1 hr. (NT)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Time: Days

Restoration Time (hrs.)	Grex 50-050[a] Deformation Angle (°) for restoration (storage) at			Alathon 15 Deformation Angle (°) restoration (storage) at	
	Ambient	-10 to -15°C.	-78°C.	Ambient	-10 to -15°C.
0	180	180	180	180	180
1	115	-	180	115	140
2	110	-	180	110	140
16	100	-	180	105	140
24	95	-	180	100	140
87	90	-	180	100	140
240	-	165	180	-	-

[a] After storage at -15°C. or -78°C. for 10 days, the polyethylene specimens (Grex 50-050) restore to essential completion in < 1 minute at 140°C.

4.1.1.7 Moulding and Extrusion-Induced Memory

Moulding and extrusion-induced memory are well-known phenomena in polyethylene and a number of other polymers.[22-26] Thus, the extrusion or moulding of polymers under certain conditions can lead to fabricated materials which are "strained" or "stressed." Subsequently, these relieve themselves of their unstable situations and, thus, give rise to distorted and deformed materials.

The moulded materials studied in this work did not exhibit any memory effects due to the moulding process. However, extrusion-induced memory was observed to be a complicating factor for extruded Alathons 7010 and 7030 and Marlex 5003. Thus, attempts to T deform extruded, unirradiated Alathons 7010 and 7030 were abortive, and resulted in shrinkage (if the specimen was cut parallel to the line of extrusion) or elongation (if the specimen were cut perpendicular to the line of extrusion). NT deformations could be performed without complication; however, restoration of these specimens resulted in shrinkage or elongation analogous to the T deformation attempts.

Irradiated (61 Mrads) specimens of Alathon 7010 and 7030 were successfully T and NT deformed without the occurrence of shrinkage or elongation. However, these deformed specimens did not restore to their exact undeformed shape; specimens cut parallel to the line of extrusion formed a "C"-shaped arc and shrunk approximately 50% in width while specimens cut perpendicular to the line of extrusion formed a wider arc and did not appear to shrink.

Unirradiated, extruded Marlex 5003 also exhibited extrusion-induced memory on heating (in attempts to T deform or restore) but the effect was less pronounced. Specimens of Marlex 5003 irradiated to 61 Mrads did not exhibit the extrusion memory phenomenon and their behavior was normal. Thus, it appears that the extrusion process can be controlled (Marlex 5003 vs. Alathons 7010 and 7030) so as to minimize the effect. Furthermore, irradiation counteracts the extrusion memory to a large extent.

The strains and stresses (memory) of polymers induced by the processing (moulding or extrusion) conditions are capable of being relieved by thermal annealing procedures. Such procedures have been discussed by various workers.[25,27] We have also accomplished this result in various other studies at RAI.

4.1.1.8 Deformation-Restoration Recycling

It was of interest to determine if the memory of a polymer specimen is retained if the specimen is subjected to a recycling of the deformation-restoration process. Grex 50-050 was tested for this purpose employing standard T deformation conditions and standard restoration conditions. It was found that a single specimen could be subjected to the deformation-restoration process a number of times without loss of the memory property; complete restoration was always observed. The maximum number of deformation-restoration cycles performed with a single specimen was ten.

4.1.1.9 Odd-Shaped Specimens

Some memory experiments were performed with specimens other than polyethylene sheet. Various odd-shaped polyethylene objects such as cylinders, cones, spheres and toys (see Figure 4.5) were tested employing standard T deformation conditions and standard restoration conditions. It was observed that these

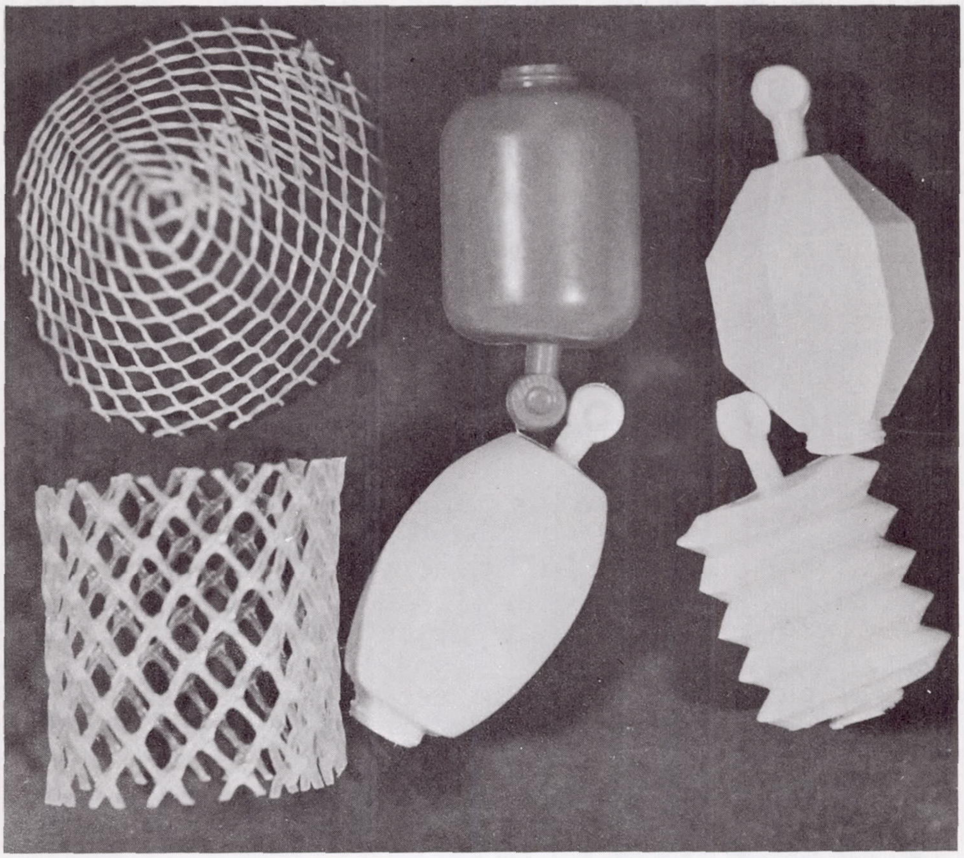

FIGURE 4.5   Various Polyethylene Shapes

specimens always restored to their original, undeformed shape (i.e., the shape they possessed during irradiation). Restoration was also accomplished by the use of the heat from infrared lamps.

4.1.1.10 Memory Loss Phenomena

The memory of deformed irradiated polyethylene specimens was observed to disappear under certain conditions. Two phenomena of "memory loss" were observed-one involving the conversion of NT deformation memory to T memory and the other, the complete disappearance of T deformation memory.

The conversion of NT memory to T memory occurred when NT deformed specimens were placed in the restoration bath (140°C.) but prevented from restoring by external forces. This was observed during work on the measurement of restoration forces (Section 4.1.2). Thus, standard NT deformed Grex 50-050 specimens could readily be prevented from restoring while in the restoration bath (140°C.) by placing a greater mass on top of the specimen than could be moved. When this was done, restoration could no longer occur. When part of this excess mass was later removed, the normal expected NT deformation restoring force was no longer present. The restoring force under these conditions is equivalent to that observed under T deformation. For restoration to occur with the manifestation of the large restoring force, it is essential that no impediment to this restoration be present initially.

The complete loss of T deformation memory was observed when T deformed specimens (or NT deformed specimens which became converted to T deformed specimens) were placed in the restoration bath but prevented from restoring by means of external forces. Thus, 123 Mrad Marlex 5003 specimens were T deformed under standard conditions (deformation angle = 180°), clamped with ordinary laboratory pinch clamps to prevent restoration, placed in a bath at 145°C. for various time intervals, the clamps then removed and the behavior of the deformed specimens in a restoration bath subsequently observed. Loss of partial T deformation memory of the specimens was observed after a few hours while complete loss was not observed even after a time interval of 1 week. Thus, deformed specimens which were prevented from restoring while in the 145°C. bath for 4-1/2 hours subsequently restored to a deformation angle of 10° while 1 week specimens restored to a deformation angle of 90°.

It should be noted, obviously, that neither the NT to T memory conversion or the complete loss of T memory would interfere with the application of the memory effect to space erectable structures. In practice, one would not attach loads to a space structure which are greater than the loads which could be moved by the structure. Thus, neither of the above memory loss phenomena would be encountered.

4.1.2 Restoring Force

The restoring force of irradiated, deformed polyethylene has been studied as a function of deformation conditions, restoration conditions, radiation dose, polymer density, initial molecular weight, quenching conditions, moulding conditions, specimen thickness and filler presence. The results are discussed below.

4.1.2.1 Deformation Conditions

The effect of deformation conditions on restoring force was studied over the 40-140°C. range. For the bulk of this work, sufficient time was allowed during deformation so as to obtain thermal equilibrium between the test specimen and environment. A small amount of work was performed under conditions of non-thermal equilibrium between specimen and environment.

It was observed that the restoring force is highly dependent upon the deformation conditions. If the deformation temperature is low, the restoring force is relatively high. As the deformation temperature is increased, the restoring force decreases. When the deformation temperature is high enough so that transparency occurs, the restoring force is at a minimum. These results are tabulated in Table 4.9 and shown graphically in Figure 4.6. The results indicate not only a decrease in restoring force with increasing deformation temperature, but also that the greatest decrease occurs as the T_m is approached.

Table 4.9

Deformation Temperature Effect on Restoring Force

Polyethylene Grade:	Moulded Grex 50-050
Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil
Radiation Dose:	61 Mrads
Deformation:	1 hour
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Restoration Temp.:	140°C.
Restoration Time:	to 5 minutes
Mass-Apex Distance:	2.5 cm.

	61 Mrads		0 Mrad Control	
	Restoring Force		Restoring Force	
Deformation Temp. (°C.)	Mass (gm.)	Moment (gm.-cm.)	Mass (gm.)	Moment (gm.-cm.)
40	170	415	-	-
60	150	370	135	330
80	125	315	90	225
100	105	250	68	170
120	65	165	38	95
140	2	5	melts in deformation environment	

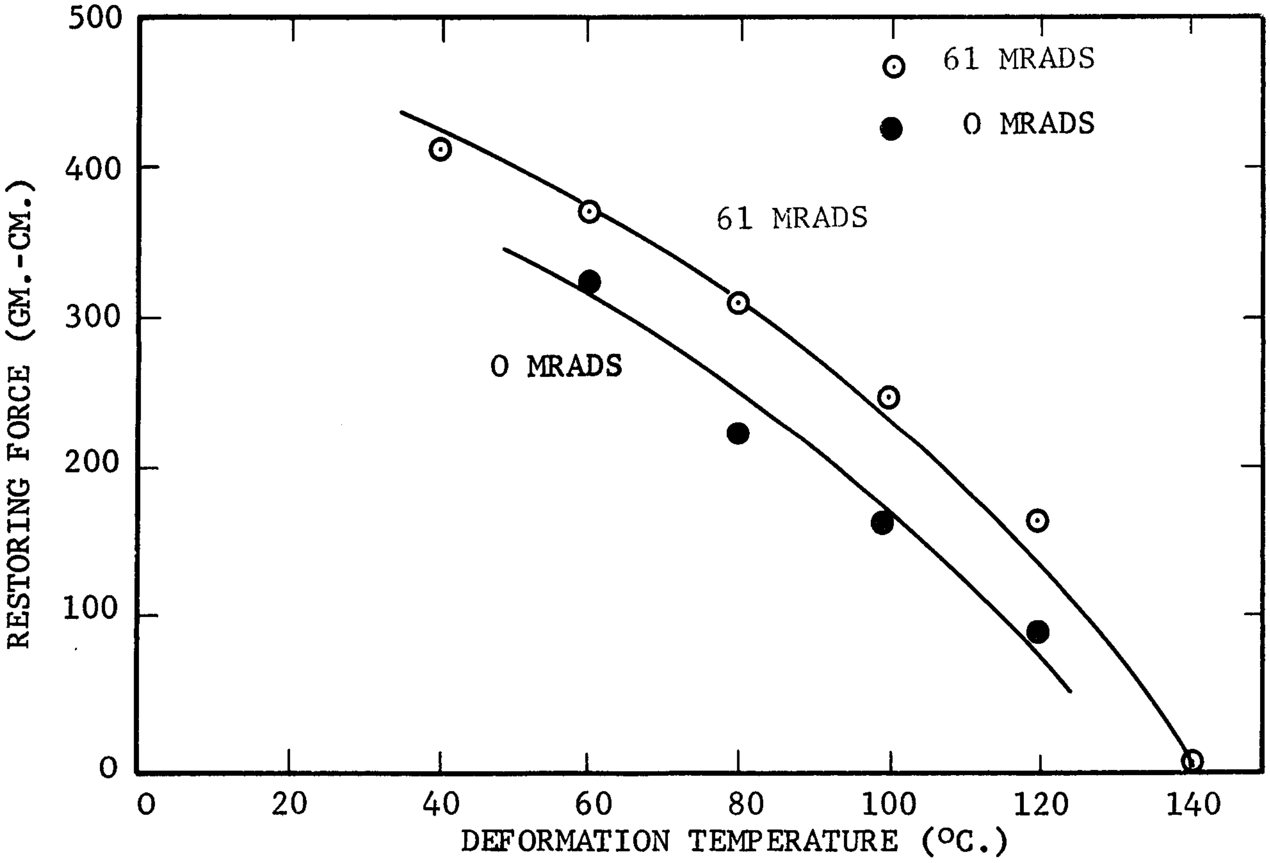

FIGURE 4.6 Deformation Temperature Effect on Restoring Force of Grex 50-050

Unirradiated polyethylene could also be tested under standard NT deformation conditions. The results (Table 4.9) show that restoration with the manifestation of relatively large forces can occur. However, for each deformation temperature, the restoring force is less than for the 61 Mrad polyethylene. In addition, test specimens melt at the deformation temperature at 140°C. The melting that, presumably, occurs upon restoration at 140°C. is not a factor since restoration occurs rapidly, before thermal equilibrium between the test specimen and environment has occurred.

Deformation employing non-thermal equilibrium between the specimen and its surroundings was performed by heating above the normal polymer T_m, removing from the hot environment after various time intervals and quenching. The degree of crystalline melting (and recrystallization) that occurs is proportional to the time in the deformation environment. This effect manifests itself in the restoring force measurement and is indicated below in Table 4.10 and Figure 4.7. Although standard conditions are not employed, the effect is nevertheless clear. Maximum restoring force occurs when a minimal amount of crystalline melting has occurred prior to deformation. As the deformation time is increased, the restoring force decreases; it reaches a minimum at transparency deformation. Prolonged deformation time after transparency has developed does not affect the restoring force.

Table 4.10

Deformation Time Effect on Restoring Force

Polyethylene Grade:	Moulded Alathon 14
Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil
Radiation Dose:	61 Mrads
Deformation:	140°C.
Deformation Angle:	180°
Deformation Quench:	10°C./10 sec.
Restoration Temp.:	105°C.
Restoration Time:	to 3 minutes
Mass-Apex Distance:	1.75 cm.

Deformation Time (sec.)	Deformation Nature	Restoring Force	
		Mass (gm.)	Moment (gm.-cm.)
5	NT	25	44
10	NT	23	40
20	T	5.5	9.6
30	T	6.0	10.5
100	T	6.0	10.5

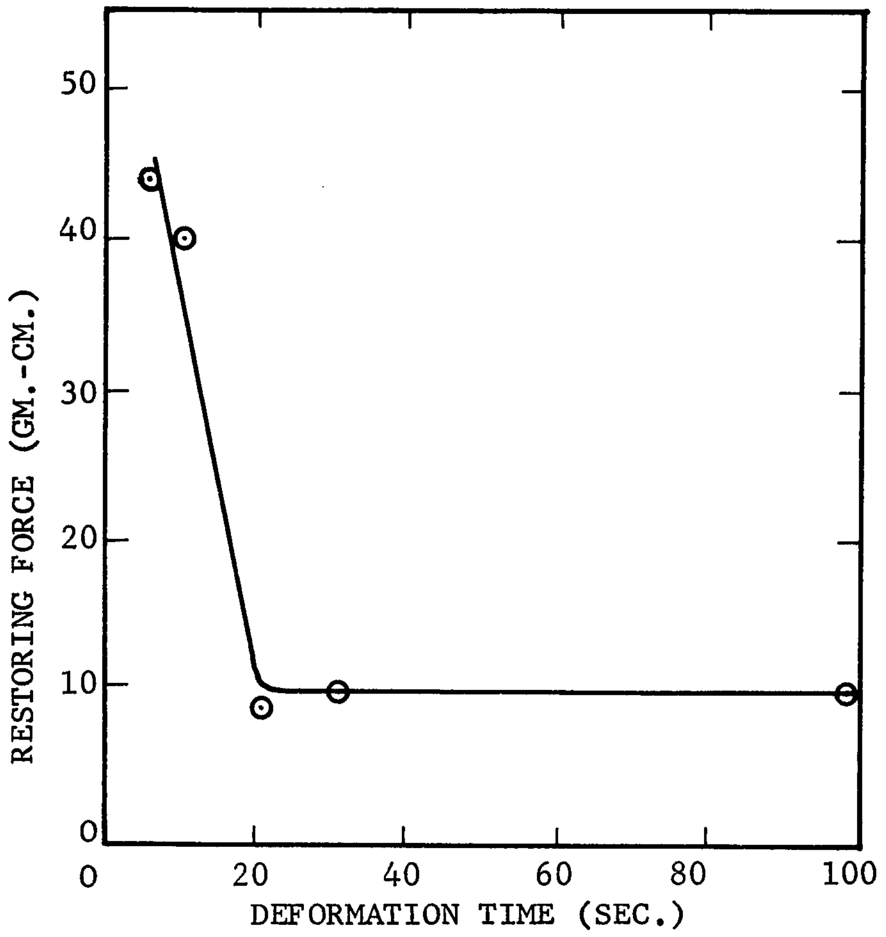

FIGURE 4.7 Deformation Time Effect on Restoring Force

4.1.2.2 Restoration Conditions

The effect of restoration conditions on restoring force was studied over the 80-140°C. range for time intervals stretching from several seconds to several hours. These conditions were chosen for the following reasons: (a) Temperatures lower than 80°C. offer no practical value. (The lower the restoration temperature, the less the degree of restoration for NT deformation; see Section 4.1.1.2.) (b) The maintenance of the test specimens at elevated temperatures for periods longer than that required to attain thermal equilibrium with its environment was unnecessary. In actual practice, restoration at 80-140°C. after standard NT deformation occurred in less than 5 seconds; restoration after T deformation occurred only at the T_m temperature and required several minutes. Tests run for intervals of hours were performed solely to ascertain positive results.

At 140°C., the restoring force of standard NT deformed specimens was about 315 gm.-cm. At 80°C., the resultant restoring force was observed to be about 300 gm.-cm. This difference is within experimental error. It is concluded, therefore, that no discernible difference in restoring force occurs at the lower restoration temperature.

The restoration temperature effect on restoring force after standard transparency deformation conditions was not considered for study since restoration does not occur unless the restoration temperature is in the vicinity of the normal polymer T_m.

4.1.2.3 Radiation Dose

The effect of radiation dose on the restoring force of Grex 50-050 was studied at various deformation temperatures, over the dose range of 12 to 245 Mrads. Higher doses were not tested because of the brittleness of specimens at the 245 Mrad dose. Lower doses were not investigated in view of the incomplete degree of restoration at approximately 5 Mrads. (See Section 4.1.1.3.) The results (Table 4.11 and Figures 4.8 and 4.9) indicate an increasing restoring force with radiation dose (it should be recalled that unirradiated deformed specimens can be restored sufficiently to measure the restoring force, but that restoration is not complete). Furthermore, decreasing the deformation temperature increases the restoring force over the entire dose range. Cracking of specimens was a problem when the radiation dose was high (245 Mrads) or the deformation temperature low (40°C.).

The effect of radiation dose on the restoring force of the low density polyethylene grade, Alathon 15, was studied in a manner similar to that of the Grex 50-050 (high density polyethylene). The results, shown in Table 4.12 and Figures 4.10 and 4.11 indicate that

(1) The restoring force of Alathon 15 decreases with increasing deformation temperature regardless of radiation dose.

(2) The restoring force of Alathon 15 increases slightly with increasing dose.

(3) The restoring force of Alathon 15 was inferior to that of Grex 50-050 under all equivalent temperature con-

Table 4.11

Radiation Dose and Deformation Temperature Effects on Restoring Force

Polyethylene Grade:	Moulded Grex 50-050
Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil
Deformation:	1 hour
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Restoration Temp.:	140°C.
Mass-Apex Distance:	2.5 cm.

Radiation Dose (Mrads)	Deformation Temp. (°C.)	Restoring Force Mass (gm.)	Restoring Force Moment (gm.-cm.)
0	60	135	330
	80	90	225
	100	68	170
	120	38	95
	140	melts in deformation environment	
12	60	140	350
	80	102	250
	100	70	175
	120	44	110
	140	0.5	1.5
61	60	150	370
	80	125	315
	100	105	250
	120	65	165
	140	2.0	5
123	60	175	430
	80	140	350
	100	130	320
	120	70	175
	140	9.3	23
245	60	samples crack on attempted deformation	
	80	samples crack on attempted deformation	
	100	samples crack on attempted deformation	
	120	74	185
	140	24	58

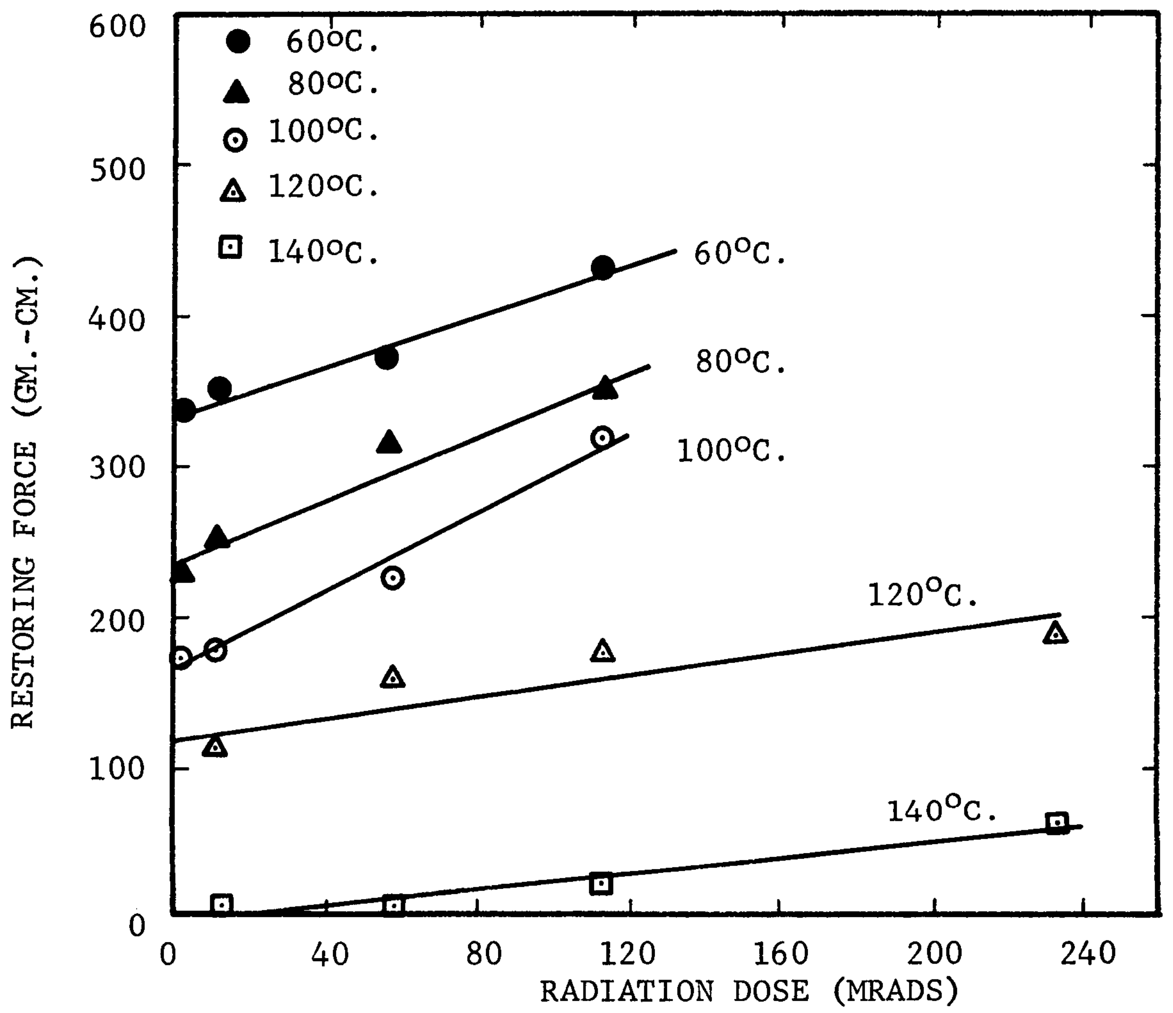

FIGURE 4.8 Radiation Dose Effect on Restoring Force of Grex 50-050 at various Deformation Temperatures

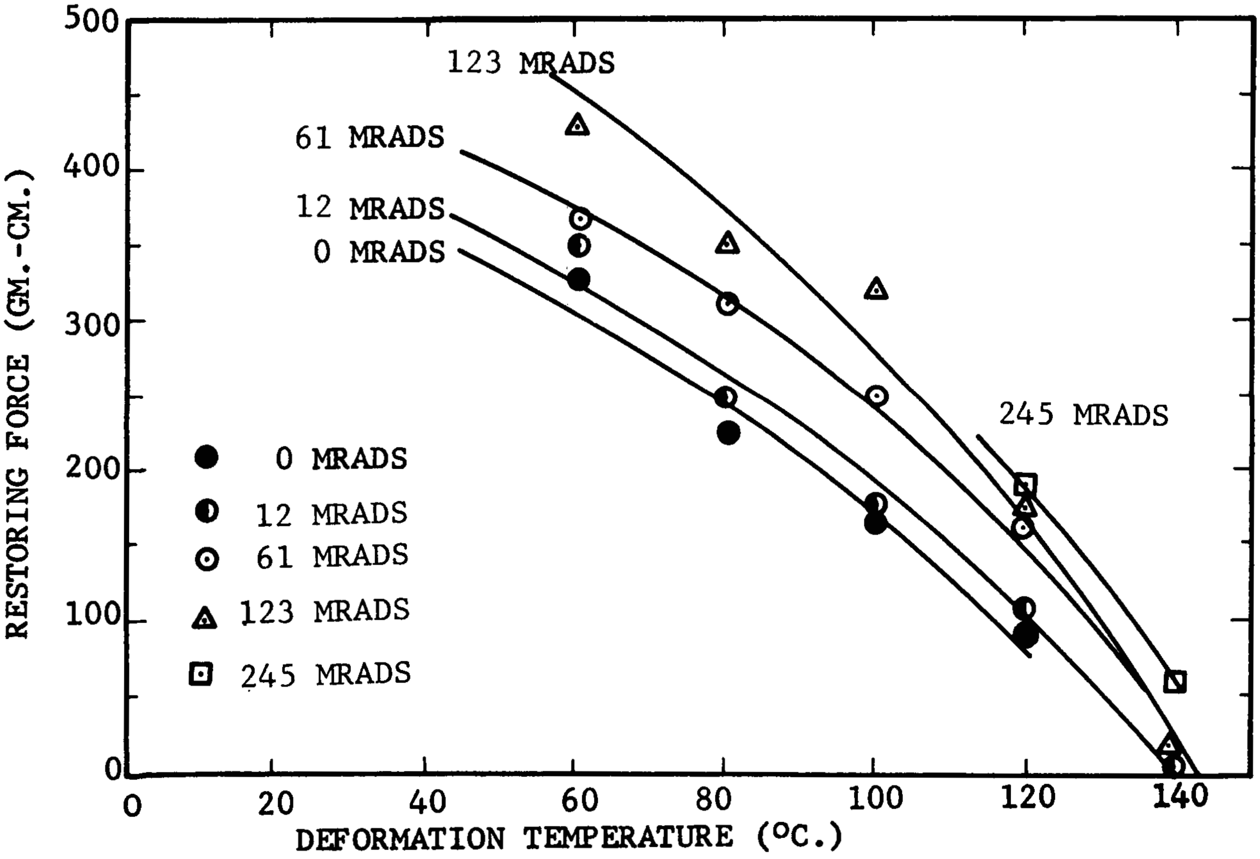

FIGURE 4.9 Deformation Temperature Effect on Restoring Force of Grex 50-050 at various Radiation Doses

Table 4.12

Radiation Dose and Deformation Temperature Effects on Restoring Force

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Polyethylene Grade: Extruded Alathon 15
Sample Dimensions: 1 cm. x 7 cm. x 52 mil
Deformation: 1 hr.
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Temp.: 140°C.
Restoration Time: to 5 minutes
Mass-Apex Distance: 2.5 cm.

Radiation Dose (Mrads)	Deformation Temp. (°C.)	Restoring Force Mass (gm.)	Moment (gm.-cm.)
0	40	42	105
	60	32	80
	80	29	72
	100	11	27
	120	specimen melts in deformation environment	
	140	specimen melts in deformation environment	
12	40	56	140
	100	18	45
	120	1	2.5
61	40	48	120
	60	39	97
	80	42	105
	100	18	45
	120	6	15
123	40	44	110
	60	41	102
	80	36	90
	100	10	25
	120	6.7	17
184	40	86	215
	60	74	185
	80	37	92
	100	12.5	31
	120	5.6	14
245	40	99	248
	62	88	220
	80	45	112
	100	14	35
	120	9.4	23

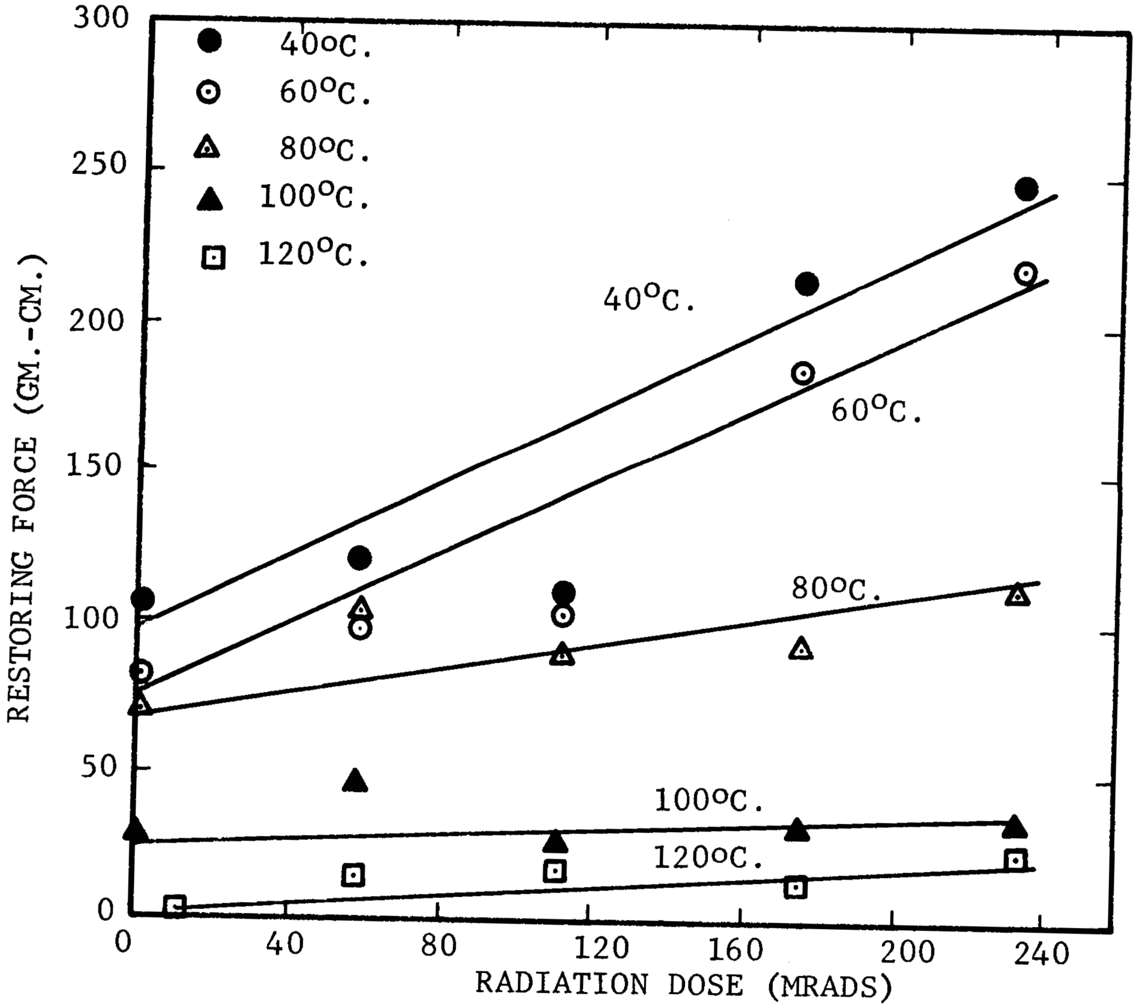

FIGURE 4.10 Radiation Dose Effect on Restoring Force of Alathon 15 at various Deformation Temperatures

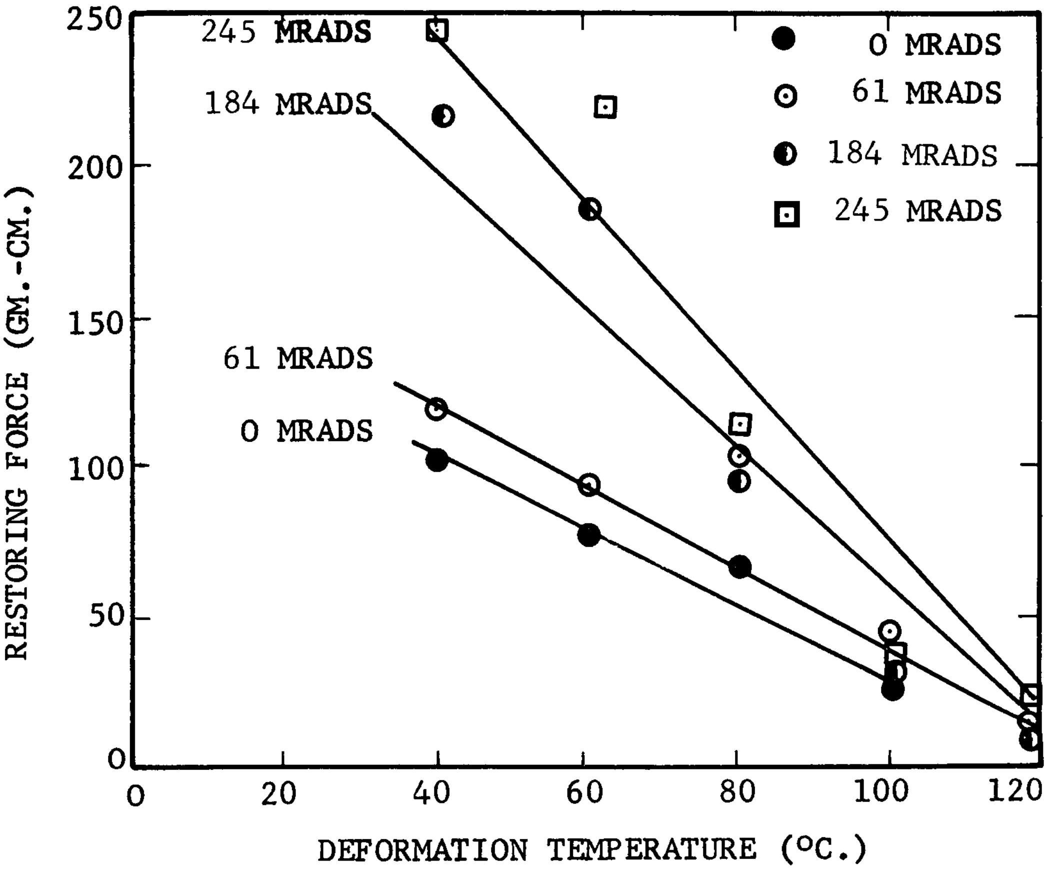

FIGURE 4.11 Deformation Temperature Effect on Restoring Force of Alathon 15 at various Radiation Doses

ditions of NT deformation.

(4) The restoring force of 61 Mrad Alathon 15, after T deformation, was slightly greater than that of 61 Mrad Grex 50-050. (This phenomenon can be explained on the basis of different initial molecular weights and is discussed in Section 4.1.2.5.)

(5) Unirradiated Alathon 15 behaves similar to unirradiated Grex 50-050. Partial restoration occurs and is followed by melting.

4.1.2.4 Crystallinity

The effect of polyethylene crystallinity on the restoring force was determined employing nine different grades of polyethylene with varying density and crystalline melting point. Along with 61 Mrad polymer tested under standard NT conditions, unirradiated controls were also run. The results of these tests, shown in Table 4.13 and Fig. 4.12, indicate that the restoring force increases with increasing crystalline melting point and density (both of which are measures of crystallinity).

It should be noted that the point for Hi-Fax 1901 in Figure 4.12 would not deviate as much from the straight line if crystalline melting point instead of density were plotted against restoring force. This deviation is due to the rather high crystalline melting point of Hi-Fax 1901 in relation to its medium density. Of course, the best parameter to plot against restoring force would be crystallinity; however, such data was not generally available. The other deviations from the straight line plot in Figure 4.12 may be explained by assuming that initial molecular weight or crosslink density is a contributing factor to the restoring force.

Table 4.13

Density Effect on Restoring Force

Moulded[a]
Sample Dimensions: 1 cm. x 7 cm. x 55-60 mil
Radiation Dose: 61 Mrads
Deformation: 80°C./1 hr. (NT)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Temp.: 140°C.
Restoration Time: to 5 minutes
Mass-Apex Distance: 2.5 cm.

			Restoring Force 61 Mrads		Restoring Force 0 Mrad Control	
Polymer	Density (gm./cc.)	T_m (°C.)	Mass (gm.)	Moment (gm.-cm.)	Mass (gm.)	Moment (gm.-cm.)
Marlex 6002	0.960	127	178	440	97	240
Alathon 7511	0.960	132-135	150	375	127	310
Alathon 7040	0.957	132-135	192	470	145	360
Marlex 5003	0.950	124	155	380	93	230
Grex 50-025	0.950	131-132	133	330	97	240
Grex 50-050	0.950	131-133	130	320	90	225
Hi-Fax 1901	0.939	129-131	237	580	114	280
Alathon 15	0.917	111	43	105	29	71
Alathon 14	0.914	108	47	115	37	92

[a] Alathon 15 samples were extruded tape.

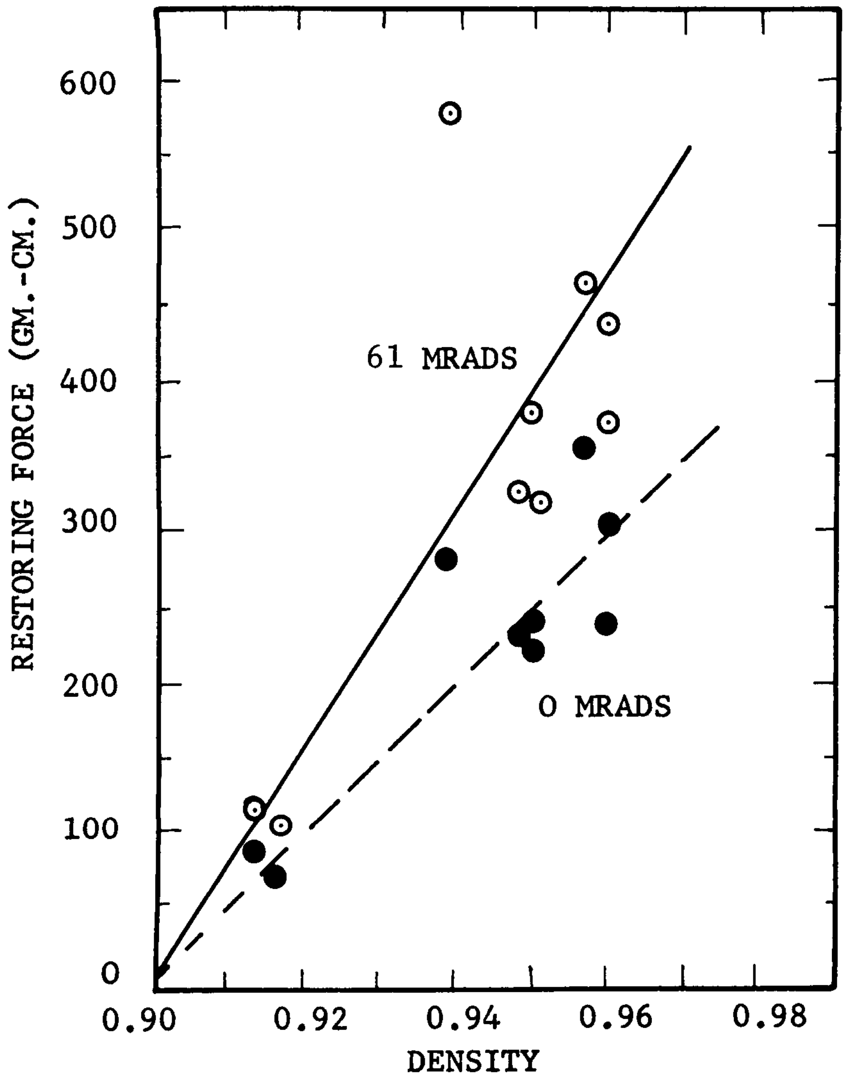

FIGURE 4.12 Density Effect on Restoring Force

4.1.2.5 Initial Molecular Weight

The effect of polyethylene initial molecular weight (i.e., $\overline{M}_n$ or $\overline{M}_w$ prior to irradiation) on restoring force has been investigated by studying nine different polyethylene grades under T deformation conditions. Since T deformation causes complete crystalline melting prior to deformation, almost complete crystalline melting prior to restoration is assured. This experimental approach means that polyethylene crystallinity plays only a minor role, if any, in the restoring force and the latter will be related solely to the crosslink density and molecular weight. Samples irradiated to identical doses should have different crosslink densities depending upon the initial molecular weight and molecular weight distributions.

The results of these tests indicate an increasing restoring force with increasing dose. Regardless of molecular weight, the absolute values of restoring force remain small compared to values obtained via NT deformation conditions. The results are given in Table 4.14 and Figure 4.13. Although the absolute values are quite small, the trend is important.

Table 4.14

Molecular Weight Effect on Restoring Force

Moulded Samples[a]
Sample Dimensions: 1 cm. x 7 cm. x 55-60 mil
Radiation Dose: 61 Mrads
Deformation: 140°C./1 hr. (T)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Temp.: 140°C.
Restoration Time: to 5 minutes
Mass-Apex Distance: 2.5 cm.

Polymer	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	Restoring Force	
			Mass (gm.)	Moment (gm.-cm.)
Grex 50-050	70-80	6-7	2	5
Alathon 7040	88	11-12	2.5	6.3
Alathon 7511	150-175	15-20	3.5	8.5
Marlex 6002	171	14	3.5	8.5
Marlex 5003	188	11	5	12
Alathon 15	500	15-20	5.5	13.5
Alathon 14	800-1000	22-26	4.0	10
Hi-Fax 1901	>2000	-	22	54

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[a] Alathon 15 samples were extruded tape.

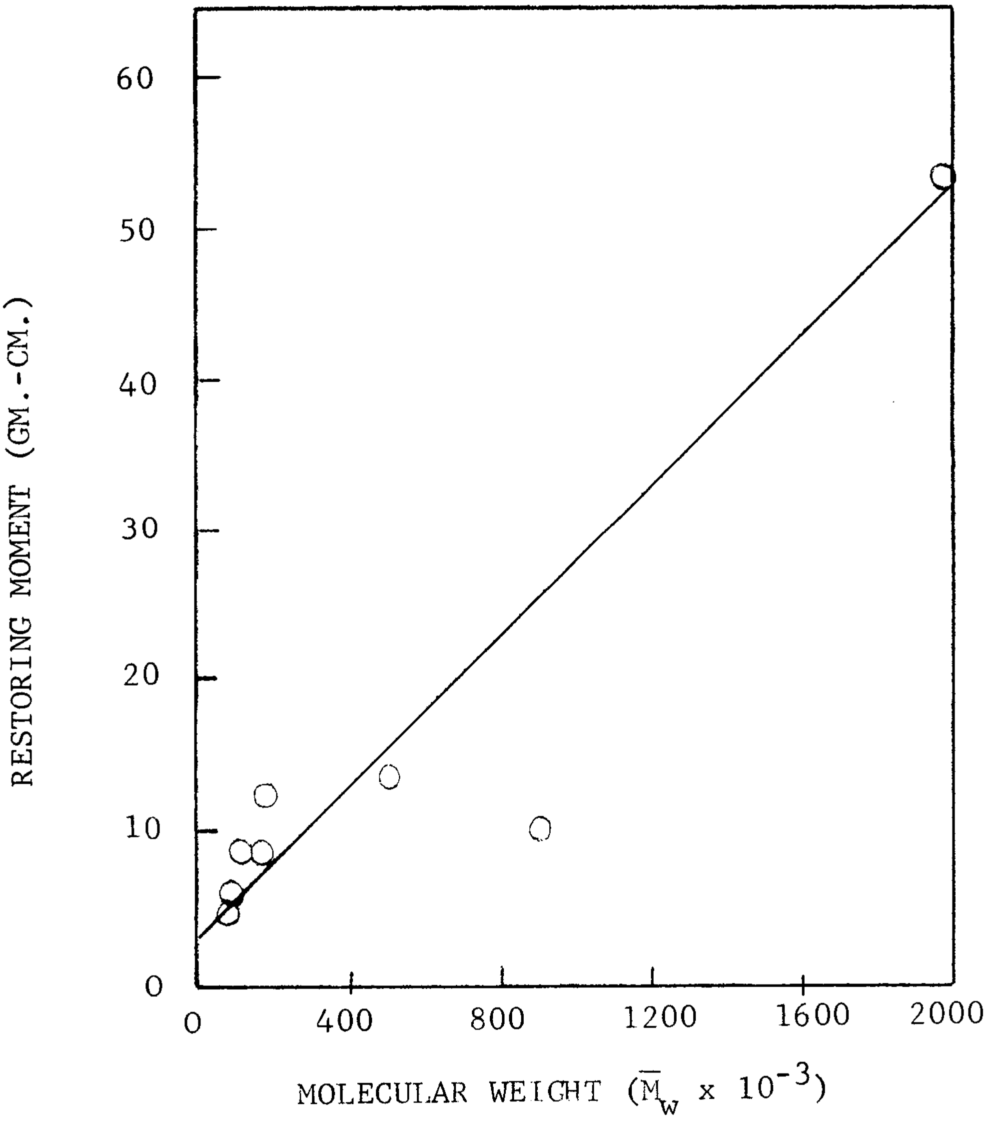

FIGURE 4.13 Molecular Weight Effect on Restoring Force

4.1.2.6 Polyethylene Thickness

It is to be expected that the restoring force (or the restoring moment) will be influenced by the film thickness. The thicker the deformed region, the greater the ability to move a specific mass. This has been investigated employing Grex 50-050 of various thicknesses ranging from 20-65 mil deformed under standard NT conditions and two other widely different, but convenient, deformation temperatures. This was done to determine whether the thickness effect varied with different deformation temperatures. (Transparency deformation conditions were avoided as the restoring forces after T deformation are very small with the material employed.) The results of these tests are shown in Table 4.15.

Table 4.15

Thickness Effect on Restoring Force

Polyethylene Grade:	Moulded Grex 50-050
Sample Dimensions:	1 cm. x 7 cm.
Radiation Dose:	61 Mrads
Deformation:	1 hour
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Mass-Apex Distance:	2.5 cm.

Deformation Temperature (°C.)	Thickness (mil)	Restoring Force Mass (gm.)	Restoring Force Moment (gm.-cm.)
68	65	187	460
	57	150	365
	44	80	200
	24	24	55
80	57	125	315
	44	64	160
	27	27	67
	20	12	30
100	67	99	245
	47	53	130
	28	16	40
	21	5	12

The results (see Figure 4.14) indicate an increasing restoring force with thickness. The exact relationship between the two parameters (restoring force and thickness) may be more clearly seen from the log-log plot in Figure 4.15. This shows that the dependent and independent variables behave as described by $y = x^a$, where a is approximately 2. The restoring force, thus, depends on the approximate square of the sample thickness. Furthermore, it is seen that this relationship holds for all three deformation temperatures studied. This relationship was obtained from restoring force measurements over the 20-60 mil range, a factor of about 3. At the lower level of thickness, the accuracy of the measurement decreases and it is not possible to obtain good data at smaller thicknesses. It may not be valid to assume that this same relationship holds true over the 1-20 mil thickness range (a 20-fold difference) and no attempt has been made to convert the data obtained throughout this project to that of 1 mil thickness.

4.1.2.7 Quenching Conditions

After the polyethylene has been deformed it is placed in a water bath at 15°C. for 15 seconds, during which time recrystallization of the melted regions occurs. If the deformation was performed under T conditions, complete recrystallization must occur; if the deformation was performed under NT conditions, only partial recrystallization will occur, the extent and nature depending upon the temperature during deformation. The 15 second interval in the quenching environment was sufficient to allow transparent samples to again become opaque and rigid (i.e., recrystallize).

Since the nature of the cooling process is, presumably,

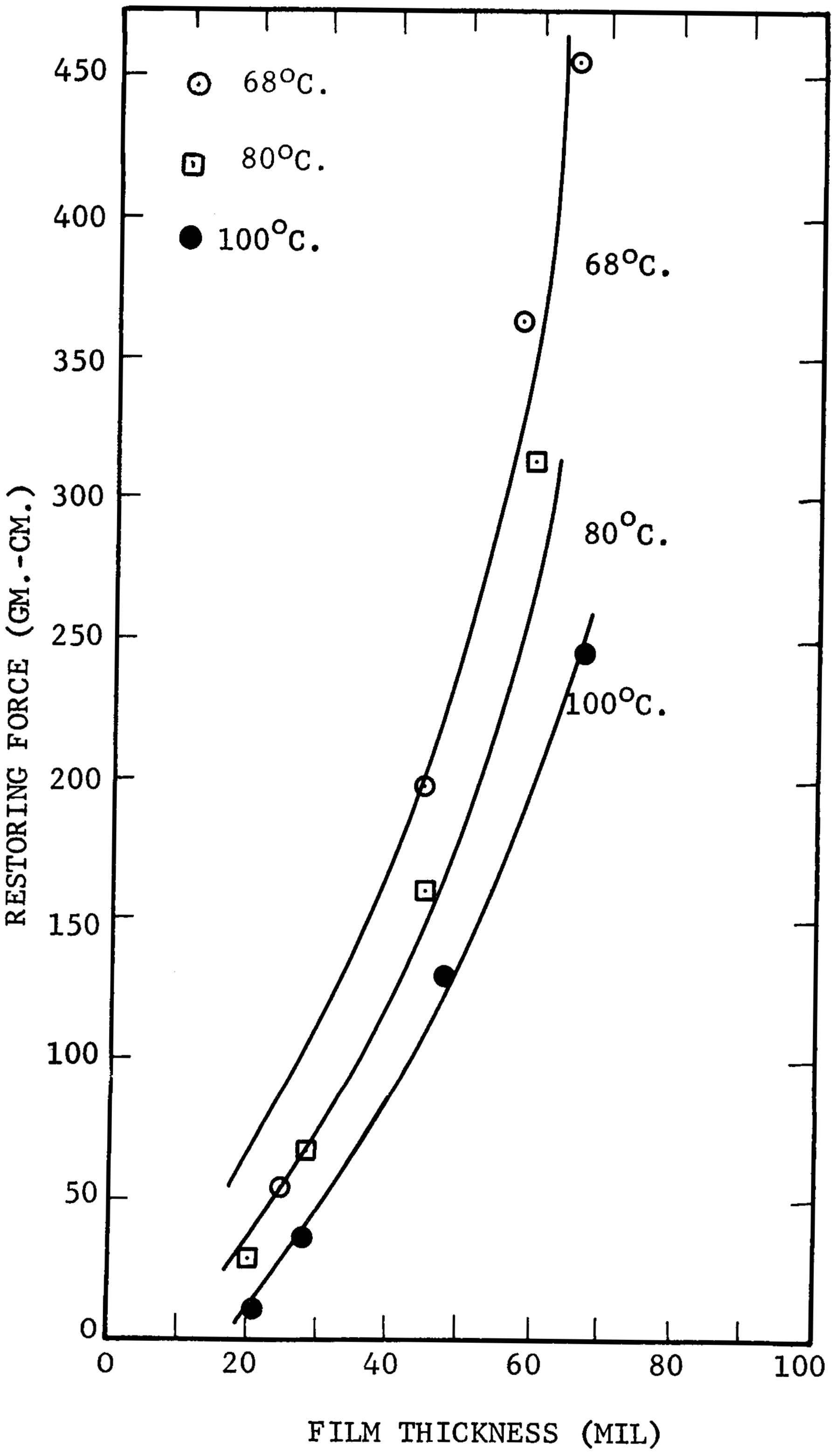

FIGURE 4.14 Thickness Effect on Restoring Force of Grex 50-050 at various Deformation Temperatures

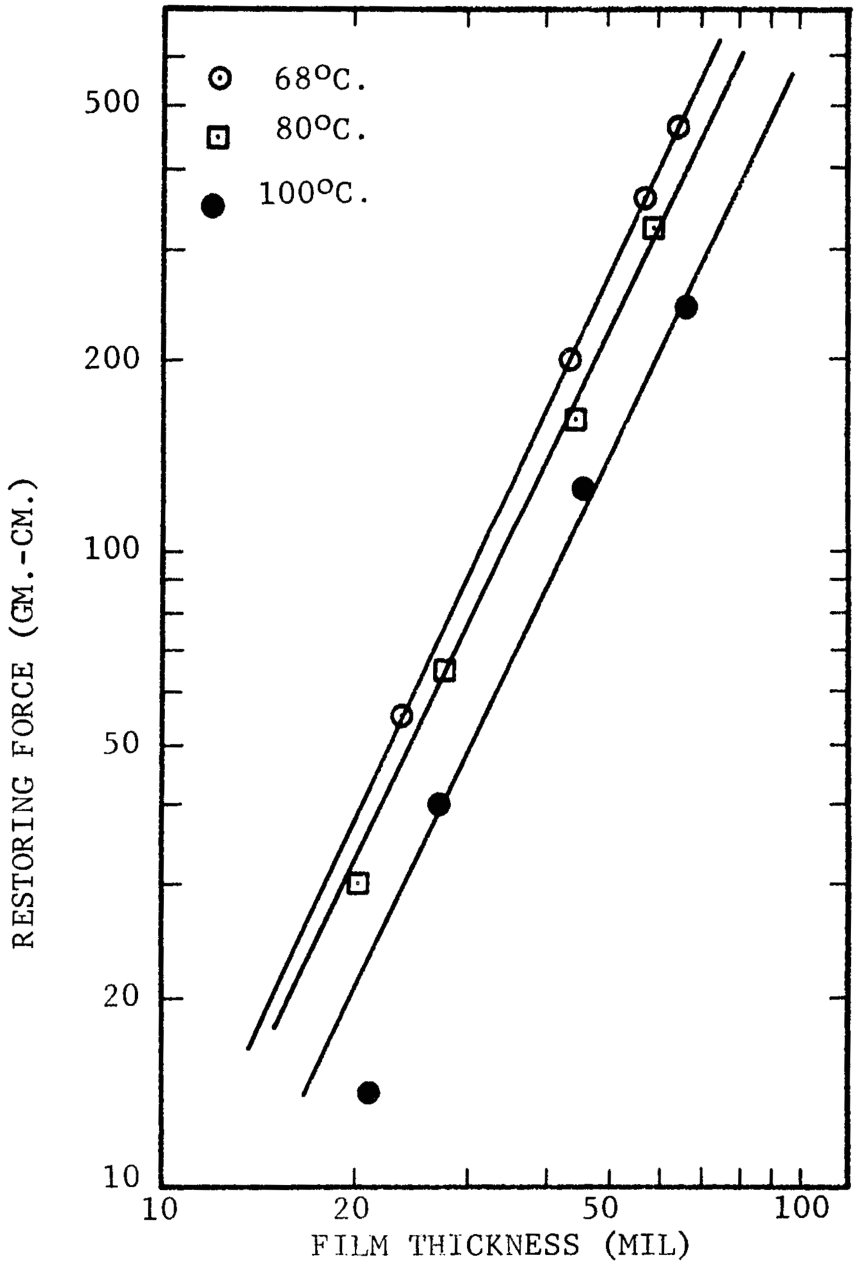

FIGURE 4.15 Thickness Effect on Restoring Force of Grex 50-050 at various Deformation Temperatures

related to the size and nature of the crystallite and spherulite formation,[3] it was deemed of importance to determine whether changing this parameter would produce a measurable change in the restoring force. Accordingly, the effect of cooling after deformation was investigated, employing otherwise standard conditions. The techniques employed were:

(a) Standard conditions: Cooling at 15°C. for 15 seconds in water bath.

(b) Cooling at ambient (room) temperature for 5 minutes.

(c) Cooling in an acetone-dry ice bath at -78°C.

Measurement of the restoring force after each set of conditions gave, respectively, 315, 275 and 275 gm-cm. It appears, therefore, that rapid or slow cooling has a rather small effect on restoring force, particularly when compared to the effects of deformation conditions or radiation dose.

4.1.2.8 Deformation Angle

Attempts were made to measure the effect of the deformation angle on restoring force employing standard NT conditions. Data was not reproducible (due to the fast onset of restoration for NT deformed specimens), although qualitative results indicate that the restoring force increases with increasing deformation angle.

4.1.2.9 Moulding Conditions

The techniques employed for moulding polyethylene sheets are described in Section 2.2. This method involves a rapid quench of the final product, and, therefore, the polyethylene will be composed of relatively uniform small crystallites. It was of interest to determine the effect of slow cooling from the melt which would result in larger, less uniform crystallites upon NT deformation.

By cooling the sheet from the melt during a 16 hour period, and deforming it under standard NT deformation conditions, no significant change in the restoring moment of Grex 50-050 could be observed; the value remained 300-315 gm-cm. This factor was, therefore, not investigated further.

4.1.2.10 Filler Effect

The effect of filler on the restoring force of polyethylene was studied under standard NT and T deformation conditions. Grex 50-050 and Alathon 14, high and low density polyethylenes, respectively, were studied. The fillers studied were ZnO and $CaSiO_3$, both at the 10% level (i.e., 10% of total specimen weight being filler). Both fillers caused a significant reduction in restoring force with both polyethylene grades. The results are shown in Table 4.16.

Table 4.16

Filler Effect on Restoring Force

Polyethylene Grade:	Moulded Grex 50-050 and Alathon 14
Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil
Radiation Dose:	61 Mrads
Deformation:	80°C./1 hr. (NT); 40°C./5 min. (T)
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Restoration Temp.:	140°C.
Restoration Time:	to 1 hour
Mass-Apex Distance:	2.5 cm.

Filler[a]	Deformation Temp. (°C.)	Grex 50-050 Restoring Force Mass (gm.)	Grex 50-050 Restoring Force Moment (gm.-cm.)	Alathon 14 Restoring Force Mass (gm.)	Alathon 14 Restoring Force Moment (gm.-cm.)
ZnO	80	92	230	31	78
$CaSiO_3$[b]	80	66	165	34	85
None	80	125	315	48	120
ZnO	140	ca. 1	ca. 2	2	5
$CaSiO_3$[b]	140	ca. 1	ca. 2	2	5
None	140	2	5	4	10

[a] Filled samples were prepared by Gering Plastics Co., Kenilworth, New Jersey

[b] Commercially available as Wollastonite P-4

4.2 Polyethylene Copolymers with Ethyl Acrylate or Vinyl Acetate

4.2.1 Introduction

Polyethylene copolymers containing up to 23% ethyl acrylate and up to 30% vinyl acetate were investigated for the memory phenomenon. The properties of these copolymers are noted in Table 2.3. The purpose of studying these copolymers was:

(a) To determine whether these copolymers exhibit memory, and if so, whether restoration is complete.

(b) To determine whether the minimum temperature for restoration would be lower for these softer copolymers than for polyethylene itself.

(c) To compare the restoring forces with those of polyethylene homopolymers and polyethylene-butene copolymers.

The literature indicates that moulded sheets of these copolymers relative to polyethylene itself are clearer (essentially transparent) and more flexible.[28] This was the case for our moulded sheets of these copolymers. Accordingly, it has not been possible to classify deformed specimens into T and NT categories based on visual clarity observations alone. However, as indicated below, these categories may be clearly defined on the basis of polymer behavior.

It has been observed that NT deformations cannot be successfully performed with these copolymers. This has been ascertained by studying the room temperature behavior of samples deformed under standard conditions at varied temperatures. When the deformation is performed after equilibrium at, for example, 100°C., a completely deformed (i.e., bent in half) specimen results that shows no "creep". When, however, the deformation is performed at, for example, 40°C., a 180° bend cannot be obtained. The sample immediately "restores" partially. A degree of deformation appears to occur, but it is not complete.

This phenomenon probably results from the reduced crystallinity of these polyethylene copolymers. These copolymers, all containing an ester as comonomer, are rubbery in nature at room temperature. Under NT deformation, sufficient recrystallization does not occur to prevent the occurrence of the sample's memory. Under T deformation conditions, however, sufficient recrystallization of the polymer occurs after deforming. Here, the deformed specimen does not "creep" and the memory is locked in. Figure 4.16 depicts this phenomenon.

4.2.2 Degree of Restoration

When the polyethylene copolymers are evaluated employing the standard conditions for studying the homopolymers, not only does restoration occur, but the degree of restoration is always found to be complete. The following may be stated with regard to the effects of the various parameters on the degree of restoration:

(a) Deformation Conditions: No effect; results are similar to those obtained with the homopolymers.

(b) Restoration Conditions: Restoration occurs at lower temperatures than for the homopolymers. The effect is a major one and is discussed more fully in Section 4.2.2.1

(c) Radiation Dose: Over the narrow range studied (31-61 Mrads), no effect was observed on the degree of restoration. This is discussed more fully in Section 4.2.2.2.

(d) Density and Molecular Weight: These parameters

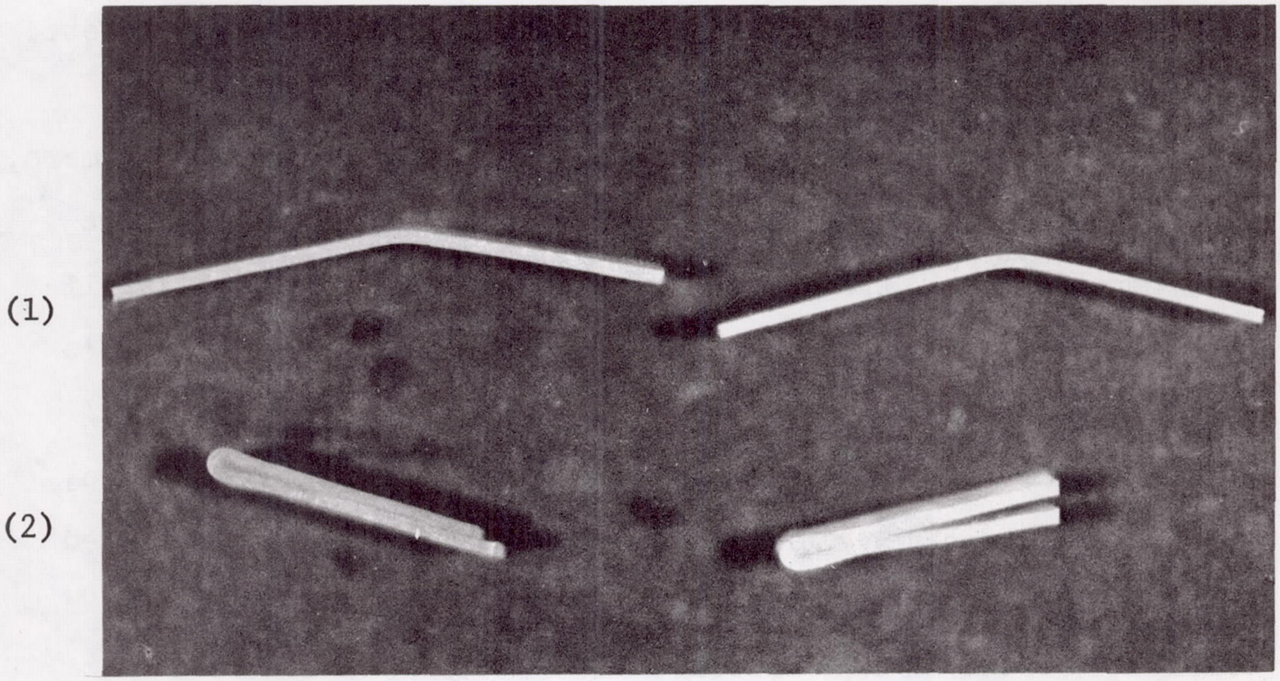

FIGURE 4.16 **NT** and T Deformation of Polyethylene Copolymers

1 = Attempted NT Deformation
2 = T Deformation

have not been studied as such with the copolymers. Their importance is not as significant as with the homopolymers.

4.2.2.1 Minimum Restoration Temperature (MRT)

The minimum temperature at which complete restoration occurs is lower than that required for low density polyethylene (Table 4.17). The latter require slightly above 100°C. The copolymers all restore to completion below 100°C. Specific temperatures required vary with the copolymer composition. DPDB-6169, DXQD-0457, and Zetafin 30 all show complete restoration in the 80-90°C. range. DQDA-3270 shows complete restoration in the 73-82°C. range, while DQDA-7268 shows complete restoration at 65°C. The co-monomer composition and melt index both increase for this series of polymers as the MRT drops (see Table 2.3).

All of these polymers fail to exhibit satisfactory NT deformations. Partial restoration always occurs (i.e., deformation angle restores to $< 180^\circ$). It is not a matter of obtaining an NT deformed specimen which shows residual creep (as do the homopolymers). In these copolymer cases, the formation of an NT deformed sample never occurs. All can be deformed under T conditions (i.e., deformation angle of 180°). In addition, DQDA-7268, after T deformation, exhibits some restoration at room temperature. This polymer has the lowest MRT (65°C.). It is possible that the crystallinity of this polymer, with almost 30% vinyl acetate, is low enough to be unable to prevent the onset of restoration at temperatures near the MRT. The results of these tests are shown in Table 4.17.

Table 4.17

Restoration Temperature Effect on Degree of Restoration of Acrylate and Acetate Copolymers

Moulded Sample Dimensions:	3-1/2 cm. x 1 cm.
Radiation Dose:	61 Mrads
Deformation:	120°C./1-3 min. (T)
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.

	Restoration Temperature					
	65°C.	73°C.	80-82°C.	88-90°C.	100°C.	
Restoration Time	Deformation Angle (°)					Comments
DPDB-6169, 120 mil						
Immediately	180	180	180		180	Complete restoration occurs above 80°C.
1-1/2 min.	-	-	-		complete	
5 min.	180	170	160			
18 hrs.	-	150	-			
43 hrs.	180	-	120			
90 hrs.	-	145	-			
DPDB-6169, 60 mil						
Immediately	180	180	180			
5 min.	180	115	80			
18 hrs.	-	95	-			
43 hrs.	180	-	40			
Zetafin 30, 60 mil						
Immediately	180	180	180			Complete restoration occurs between 80-90°C.
1 min.	-	-	complete			
5 min.	180	50				
43 hrs.	180	50				

Table 4.17 Continued

Restoration Temperature Effect on Dose of Restoration of Acrylate and Acetate Copolymers

Moulded
Sample Dimensions: 3-1/2 cm. x 1 cm.
Radiation Dose: 61 Mrads
Deformation: 120°C./1-3 min. (T)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.

	Restoration Temperature					
	65°C.	73°C.	80-82°C.	88-90°C.	100°C.	
Restoration Time	Deformation Angle (°)					Comments
DXQD 0457, 120 mil						
Immediately	180	180	180		180	Complete restoration occurs above 80°C.
1 min.	-	-	-		complete	
5 min.	160	140	80			
18 hrs.	-	100	-			
43 hrs.	140	-	55			
DQDA-3270, 120 mil						
Immediately	180	180	180	180		Complete restoration occurs between 73-82°C.
5 min.	100	60	30	complete		
18 hrs.	-	40	-			
43 hrs.	90	-	complete			
90 hrs.	-	20				
DQDA-3269, 120 mil						
Immediately	180	180	180			Complete restoration occurs between 65-73°C.
4-5 min.	90	30	complete			
18 hrs.	-	complete				
43 hrs.	55					

Table 4.17 Continued

Restoration Temperature Effect on Dose of Restoration of Acrylate and Acetate Copolymers

Moulded
Sample Dimensions: 3-1/2 cm. x 1 cm.
Radiation Dose: 61 Mrads
Deformation: 120°C./1-3 min. (T)
Deformation Angle: 180°
Deformation Quench: 15°C ./15 sec.

Restoration Time	Restoration Temperature 65°C.	73°C.	80-82°C.	88-90°C.	100°C.	Comments
	Deformation Angle (°)					
<u>DQDA-3269, 60 mil</u>						
Immediately	180	180	180			
1-1/2 min.			complete			
5 min.	90	20				
18 hrs.	-	<5				
43 hrs.	62	-				
90 hrs.	-	complete				
<u>DQDA-7268[a], 120 mil</u>						
Immediately	180	180		180		Complete restoration occurs at 65°C.
1 min.	-	-		complete		
5 min.	5	complete				
43 hrs.	complete					
<u>DQDA-7268[a], 60 mil</u>						
Immediately	180	180	180			
1-1/2 min.	-	-	complete			
5 min.	95	20				
18 hrs.	-	complete				
43 hrs.	complete					

[a] These specimens begin to restore upon storage at room temperature.

4.2.2.2 Radiation Dose

Varied radiation dose, in the narrow 31-61 Mrad range, had no effect on the degree of restoration. A similar result was observed earlier with the polyethylene homopolymers (see Table 4.18).

This parameter was not investigated further. It was noted, however, that certain of these copolymers developed "bubbles" on radiation, presumably due to the release of gases. No attempt was made to measure the amount of gas released or test the regions of the sheet that exhibited this phenomenon. Except for Epolene E-10, bubble formation did not occur with the homopolymers.

A 4.3 Mrad radiation dose was studied with DPDB-6169 and DQDA-7268. Only slight restoration of the former occurred under standard T conditions. After stretching, restoration was only partial. Qualitative observation of degree of restoration under these conditions indicated considerably poorer restoration behavior than for either Grex 50-050 or Marlex 6002 under comparable test conditions. DQDA-7268 melted in the deformation bath despite the 4.3 Mrad dose.

Table 4.18

Radiation Dose Effect on Degree of Restoration of Acrylate and Acetate Copolymers

Moulded	
Sample Dimensions:	3-1/2 cm. x 1 cm. x 60 mil
Deformation:	120°C./1-3 min. (T)
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.

Restoration Time	Dose (Mrads)	Restoration Temperature 65°C. Deformation Angle (°)	Restoration Temperature 80-85°C. Deformation Angle (°)
DPDB-6169			
Immediately	31	180	180
5 min.		180	120
43 hrs.		180	75
Immediately	61	180	180
5 min.		180	80
43 hrs.		180	40
Zetafin 30			
Immediately	31	180	180
5 min.		180	105
43 hrs.		180	90
Immediately	61	180	180
5 min.		180	50
43 hrs.		180	50
DQDA-3269			
Immediately	31	-	180
1-1/2 min.		-	complete
Immediately	61	-	180
1-1/2 min.		-	complete
DQDA-7268			
Immediately	31	-	180
2-1/2 min.		-	complete
Immediately	61	-	180
1-1/2 min.		-	complete

4.2.3 Restoring Force

The restoring forces of some polyethylene copolymers were studied, in order to obtain comparative data with the polyethylene homopolymers discussed in Section 4.1. No attempt was made to study the effect of the parameters of Section 4.1.2 on the restoring force. Restoring forces were determined only under T deformation conditions in view of the inability of these polymers to be NT deformed. The restoring forces of these copolymers are listed in Table 4.19.

Table 4.19

Restoring Forces of Acrylate and Acetate Copolymers

Moulded Sample Dimensions:	1 cm. x 7 cm. x 55-60 mil
Radiation Dose:	61 Mrads
Deformation:	120°C./1 hr. (T)
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Restoration Temp.:	140°C.
Restoration Time:	to 2 min.
Mass-Apex Distance:	2.5 cm.

	Restoring Force	
Polymer Grade	Mass (gm.)	Moment (gm.-cm.)
DPDB-6169	8-11	20-28
Zetafin 30	9-11	22-28
DQDA-3269	9-12	22-30
DQDA-7268	6-8	15-20

With these copolymers, the non-rigid behavior during the measurement of restoring force was quite apparent (see Section 3.3). Accordingly, only approximations are listed. It is of interest that the values obtained are greater than for the homopolymers under T deformation (see Section 4.1).

4.3 Vexar Polyethylene Mesh

4.3.1 Introduction

Since a grid structure would be of interest for use in space erectable structures such as communications satellites, the memory of polyethylene mesh was studied. Six grades of extruded Vexar polyethylene mesh, obtained from DuPont, were investigated. These grades, identical in chemical and physical properties to standard high, medium and low density polyethylenes, differ only in the fact that they are grid-like in nature and non-continuous. The significant physical properties of these grades are described in Table 2.2, and their appearance is seen in Figure 2.1.

In view of the similarity of the Vexar polyethylene mesh to standard polyethylenes, only those properties which might be influenced by the presence of a grid structure were studied. The degree of restoration was studied as previously described (Section 3.2.2) Minimum restoration temperature was studied only to confirm differences based on the different densities. The possible effect of extrusion-induced memory was considered and sought. Restoring forces were not measured, although the ability of these structures merely to move masses was confirmed.

4.3.2 Restoration Behavior

As with all other polyethylene homopolymers, the degree of restoration was observed to be complete at temperatures above the normal polymer T_m. The deformation conditions could not be readily characterized on the basis of visual transparency or non-transparency due to the grid structure. Standard T or NT behavior was readily discernible however; NT deformed samples showed room temperature creep and a greater degree of restoration at lower restoration temperatures. T deformed samples showed no creep and required higher restoration temperatures for the onset of restoration.

The results (Table 4.20) show the degree of restoration to be clearly defined on the basis of density and T_m as for the polyethylene sheet specimens. The results may be summarized as:

(a) NT deformed specimens (80°C.) of all grades restore to essential completion at 140°C. The event occurs over a matter of minutes.

(b) T deformed specimens (140°C.) of D 1/1-100-90, D 3/3-60-90, and D 8/8-30-90, low density polyethylenes, all restore to essential completion at 100°C., 120°C., and 140°C.

(c) T deformed specimens (140°C.) of D 4/4-30-90 and D 6/6-20-90, high density polyethylenes, restore to essential completion at 140°C., offer partial restoration at 120°C., and no restoration at 100°C.

(d) The behavior of the medium density polyethylene D 12/12-30-90 is similar to the high density, but restoration is complete at 120°C.

The degree of restoration at ambient temperatures and 65°C. was observed. As with other polyethylene grades, partial restoration occurred after NT deformation, none occurred after T deformation and where restoration did occur, it was incomplete. The results are given in Table 4.21.

Table 4.20

Restoration Temperature Effect on Degree of Restoration of Vexar Mesh

Extruded Vexar Mesh

Sample Dimensions:	4 cm. x 7 cm.
Radiation Dose:	61 Mrads
Deformation:	140°C./1 hr. (T)
Deformation Angle:	180°
Deformation Quench:	15°C./15 sec.
Restoration Time:	to 1 hour

	Restoration Temperature		
	100°C.	120°C.	140°C.
Vexar Grade	Degree of Restoration		
D 1/1-100-90	complete	complete	complete
D 3/3-60-90	complete	complete	complete
D 8/8-30-90	complete	complete	complete
D 12/12-30-90	no change	complete	complete
D 4/4-30-90	no change	partial (ca. 90°C.)	complete
D 6/6-20-90	no change	partial	complete

Table 4.21

Deformation Nature Effect on Degree of Restoration of Vexar Mesh

Extruded Vexar Mesh
Deformation: 120°C.
Deformation Angle: 180°
Deformation Quench: 10°C./15 sec.

Vexar Grade	Dose (Mrads)	Sample Dimensions (cm.)	Deformation Time (sec.)	Deformation Nature	25°C. 5 min.	Restoration 30 min.	2 hrs.	Temperature 2 days	9 days	2 wks.
					Deformation		Angle (°)			
D 1/1-100-90	31	4 x 8	3	NT	135	105		95	95	
D 1/1-100-90	31		300	T	180	180		180	180	180
D 3/3-60-90	61		3	NT	180	160	155	150		145
D 3/3-60-90	61		300	T	180	180	180	180		180
					65°C.	Restoration		Temperature		
					10 min.	1 day	3 days	1 wk.		
					Deformation		Angle (°)			
D 1/1-100-90	61	2 x 4	5	NT	180	140	130	120		
D 1/1-100-90	61		30	T	180	180	180	180		
D 1/1-100-90	245		30	T	180	180	180	180		
D 3/3-60-90	61		30	T	180	180	180	180		
D 8/8-30-90	61		3	NT	180	180	180	180		
D 8/8-30-90	61		30	T	180	180	180	180		
D 12/12-30-90	61		30	T	180	180	180	180		
D 12/12-30-90	245		30	T	180	180	180	180		
D 4/4-30-90	61		3	NT	180	100	100	90		
D 4/4-30-90	245		30	T	180	180	180	180		

The minimum restoration temperature is also controlled by the density of the mesh. Table 4.22 indicates the temperature required to cause complete restoration over a matter of minutes.

Table 4.22

Temperatures Required for Complete Restoration of Vexar Mesh

Extruded Vexar Mesh
Sample Dimensions: 4 cm. x 8 cm.
Radiation Dose: 61 Mrads
Deformation: 140°C./5 min. (T)
Deformation Angle: 180°
Deformation Quench: 15°C./15 sec.
Restoration Time: to 3 min.

Vexar Grade	Restoration Temperature for Complete Restoration (°C.)
D 1/1-100-90	100
D 3/3-60-90	100
D 8/8-30-90	100-105
D 12/12-30-90	109
D 4/4-30-90	120
D 6/6-20-90	115

Extrusion-induced memory was observed to be a complicating factor with these extruded Vexar meshes as it was with Alathons 7010 and 7030 and Marlex 5003 but not as pronounced.

5.0 SUMMARY OF RESULTS

The results of these studies on the memory of irradiated polyethylene may be summarized as follows:

5.1 Degree of Restoration

a. The deformation conditions were found to have no effect on the degree of restoration. Complete restoration occurs under a variety of deformation conditions if the restoration temperature is above the crystalline melting point of the polymer.

b. The restoration conditions are of major importance in controlling the degree of restoration of deformed polyethylene. For restoration to be complete, the polyethylene must be heated to transparency (i.e., above its normal T_m). For high density polyethylene, this temperature is ca. 130-135°C.; for low density, the required temperature is ca. 105°C. Polyethylene copolymers containing 15% or more ethyl acrylate or vinyl acetate were found to require lower minimum restoration temperatures than the homopolymers since their T_m values were lower. Thus, the various acrylate and acetate copolymers studied restored at temperatures of 65-90°C.

c. Unirradiated and irradiated polyethylene behave very similarly at deformation temperatures below T_m. Above T_m, unirradiated polyethylene melts and flows and, thus, memory cannot be observed.

d. Radiation dose does not control the degree of restoration above the minimal dose of ca. 5-10 Mrads for a polyethylene of $\overline{M}_w$ of at least 70,000.

e. Polyethylene density affects the degree of restoration only insofar as it affects the normal crystalline melting point of the polymer (see 5.1 c above). Low density grades restore to completion at lower temperatures than high density grades.

f. Initial molecular weight, above a certain minimum, is not a factor in controlling the degree of restoration; however, this is closely related to the radiation dose (see 5.1 d above). A 10 Mrad dose to a polyethylene of $\overline{M}_w$ of ca. 70,000 gives complete restoration.

g. Storage of NT deformed specimens at -78°C. will prevent creep which is common at ambient temperatures and retarded at -15°C.

h. Moulding and extrusion-induced stresses and strains in polyethylene complicate the memory effect studied on this project. Such complications can, however, be minimized by annealing techniques.

i. Vexar polyethylene mesh behaves exactly similar to polyethylene sheet as regards the memory effect.

j, The acrylate and acetate copolymers of polyethylene exhibit the memory effect as does polyethylene.

5.2 Restoration Force

a. Deformation conditions greatly influence the restoration force. NT deformed polyethylene has much greater restoration forces than T deformed polyethylene.

b. The restoring force increases with radiation dose for both T and NT deformed polyethylene.

c. The restoring force for NT deformed polyethylene increases with increasing polymer density and T_m.

d. The restoring force increases with increasing molecular weight (as measured under T deformation conditions).

e. The restoring force is proportional to the square of the polyethylene thickness for NT deformed polyethylene over the 20-60 mil thickness range.

f. Quenching and moulding conditions do not appear to affect the restoring force.

g. The presence of ZnO or $CaSiO_3$ fillers in the polyethylene prior to irradiation lowers the restoring force.

6.0 MECHANISM OF POLYETHYLENE MEMORY

The question naturally arises as to the mechanism of the memory effect of polyethylene. Any suggested mechanism must be compatible with and capable of explaining several experimental facts. The mechanism for polyethylene memory must explain the following facts:

1. The presence of two types of memory-the memory which is observed upon NT deformation and that observed upon T deformation.

2. The requirement of restoration temperatures above the crystalline melting point (T_m) of the polymer in order to obtain complete restoration. This results in an increase in restoration temperature with increasing T_m.

3. The degree of restoration dependence on the restoration temperature for NT deformations and the lack of such dependence for T deformation.

4. The increase of restoring force with decreasing deformation temperature. NT deformation yields greater restoring forces and faster restoration relative to T deformation.

5. The increase of restoring force with increased radiation dose for both T and NT deformations with the effect being greater for NT deformation, but the failure of dose to affect the degree of restoration.

6. The increase in restoring force with initial polymer molecular weight for T deformation.

Based on all the available information it is felt that a fairly comprehensive mechanism can be proposed to explain the memory of irradiated polyethylene. Our mechanism for the memory effect will be presented in terms of the crystalline-amorphous picture of polyethylene as described in Section 1.2. However, it could just as easily be presented in terms of the folded-chain theory of crystallinity. We do not wish, here, to discuss the exact nature of the crystalline polyethylene but will discuss the memory of polyethylene in terms of the disruptions and destabilizations of polymer structure which occur during deformation and of the subsequent relieving of these disruptions and destabilizations during restoration.

As was mentioned in Section 1.2, polyethylene can be thought of as consisting of crystalline and non-crystalline regions. The crystalline regions are especially characterized by high intermolecular forces of attraction between polymer chains. The structure of irradiated polyethylene (at doses below those which destroy crystallinity) is analogous to unirradiated polyethylene except for the superposition of cross-links between chains. (Irradiation of polyethylene also results in other changes such as changes in the type and concentration of unsaturation; however, these are not thought to affect the memory phenomenon.)

It is suggested that when irradiated polyethylene is deformed, the ensuing disruptions in the polymer are of two types. One is the disruption and destabilization of the crystalline regions and the other is the disruption and destabilization of the crosslinked regions. We hereby define the memory due to disrupted crystalline regions as plastic memory and that due to disrupted crosslinked regions as elastic memory. The memory observed in NT deformed polyethylene is caused by a combination of plastic and elastic memories;

that observed in T deformed polyethylene is due only to elastic memory. It should be obvious that plastic memory is inherent in polyethylene (and other polymers) and is not at all dependent on crosslinking; but only crosslinked polyethylene possesses elastic memory.

When irradiated polyethylene is deformed at NT temperatures, the deformed specimen begins to restore immediately at ambient temperatures (25°C.). In other words, NT deformations cannot be "locked in" completely...there is immediate recovery. As the NT deformation temperature increases, the restoration at ambient temperatures becomes progressively subdued and finally, when the deformation is performed above the T_m, the memory of the deformed polyethylene can be locked-in indefinitely. The reasons for the locking-in or non-locking-in of memory are based on the melting and recrystallization of various polyethylene regions during the deformation and quenching process. (It should be borne in mind at this point that polyethylene like most other polymers contains different crystalline regions which melt over a very wide range of temperatures. The T_m is only the temperature at which the last remnants of crystalline material melt.[3])

Deformation of polyethylene at temperatures above the melting point of some crystalline regions (types) results in the melting of said material during deformation followed by their recrystallization during the quenching process. These recrystallized regions in the deformed specimen are not a source of memory...they are able to align themselves into a stable configuration during the deformation process (during which they melt). Thus, the deformed specimen consists of a highly dynamic situation. The plastic/elastic memory forces are attempting to restore it to its undeformed shape. However, opposing this restoration tendency are the crystalline forces due to the recrystallization of the crystalline regions which melted during the deformation heating. These recrystallization forces will be referred to as "stabilizing" forces. The net interplay of the stabilizing and memory forces determines if restoration occurs at ambient temperatures, and the behavior of deformed specimens under various deformation and restoration temperatures.

The determining factor which influences the outcome of the interplay of the restoration and stabilizing forces is the amount of melting and recrystallization of polymer which occurs during the deformation and quenching process. As the amount of crystalline melting and recrystallization increases, the forces of stabilization increase and move in the direction of overcoming the forces of restoration. In actual practice we have observed that the plastic memory restoration forces are sufficiently high such that deformation temperatures in the vicinity of the T_m must be reached before the stabilizing forces become greater than the restoration forces and the deformed specimen does not recover. This is in line with our results which show the plastic memory restoring forces to be much larger than the elastic memory restoring forces. It should be mentioned that as the deformation temperature increases for NT deformations, the degree of restoration at ambient temperatures decreases since the stabilizing forces are increasing while the restoring forces are decreasing.

At low deformation temperatures the deformed polyethylene specimen possesses both plastic and elastic memory. As the deformation temperature is increased, the amount of plastic memory in the deformed specimen decreases since the amount of deformed crystalline region is decreasing. This is so because those crystalline regions which melt upon deformation are able to align themselves into a new, stable configuration and are not a source of strain and memory in the quenched deformed specimen. When the deformation temperature is at or above the crystalline melting point (T_m), complete melting of all crystalline regions has occurred during deformation. The resulting quenched, deformed specimen no longer contains plastic memory. The memory of such a T deformed specimen is solely due to elastic memory which is attributable to the crosslinked chains only.

It has been noted that complete crystalline melting is required in order to obtain complete restoration for both T and NT deformations. This is so for T deformation since all crystallinity must be removed in order that the elastic memory of the deformed crosslinked network be allowed to exert itself. It is also true for NT deformation because crystalline melting must occur for the deformed crystalline regions to restore themselves to completion and also for the same reason as just mentioned for T deformed specimens.

The fact that NT deformed specimens restore faster than T deformed specimens and also have greater restoration forces is attributed to the greater restoration forces of plastic memory. In other words, the disruption of crystalline regions causes a greater destabilization than does the disruption of crosslinked polymer chains.

Our experimental results have shown that both T and NT deformations give rise to increasing restoration forces with increased radiation dose. This has been, of course, attributed to the fact that crosslinking results in elastic memory and that the extent of elastic memory increases with increased radiation dosage. However, it should be noted that the incremental increase in NT restoration forces per unit radiation dose was greater than in the case of T deformation restoration forces. This would indicate that a deformed crosslink in the crystalline region comprises a much more unstable situation than a deformed crosslink in the amorphous region.

It was experimentally observed that at a given constant dose of irradiation the restoration force for T deformation increased with increasing initial polymer molecular weight. This is attributable to the fact that the polymer with the highest molecular weight will at a given dosage consist of a more highly crosslinked network and its deformation would be expected to lead to a more highly strained situation. This would give rise to higher restoration forces.

One last item worthy of mention is the memory loss which was found for both T and NT deformed specimens which were heated while in the deformed state. The conversion of NT to T deformation under these conditions is of course not anomalous, since what is simply occurring is that the NT deformed specimen, while being held in the deformed shape, undergoes crystalline melting and its behavior then is exactly analogous to the T deformed specimen. However, the loss of memory of T deformed specimens on heating in the deformed state indicates that the crosslinked polymer network is sufficiently mobile that it is able to move around and establish new stable configuration in the macroscopic deformed shape.

7.0 RECOMMENDATIONS FOR FUTURE WORK

The results of our study of the memory effect are quite encouraging and it is recommended that future work be geared to the purpose of

a. applying the phenomenon to passive communication satellites such as required for projects Echo and Rebound,

b. applying the phenomenon to objects of any shape for future potential space applications.

The requirements for the use of the memory effect for communication satellites include

1. A restoring force of the deformed object sufficient to cause restoration.
2. Complete restoration.
3. A manner of inducing heating of the deformed object to cause restoration to proceed.

Requirements for other types of space structures include those listed above and possibly another depending upon the particular end use. Thus, if one wishes to employ the polymeric memory effect to act as a switch in space, the polymeric switch would itself require the property of rigidity. This would also be a general requirement for other objects, e.g., space stations, moon shelters, antennas, etc. Thus, to the first three requirements one must also add

4. rigidization of the restored specimen.

Of these four listed requirements some have been studied and problems relating to them solved; others require further investigation.

In our study under the subject contract, RAI has investigated the radiation-induced memory effect in polyethylene and polyethylene copolymers. It has been shown that under the proper conditions essentially complete restoration can be caused to occur. The parameters that control the degree of restoration, the restoring forces that are involved, and the requirements for reducing restoration temperatures have been elucidated. In addition, methods for controlling the magnitude of the restoring force have been developed.

Furthermore, in-house work at RAI with other polymers has shown that the memory effect can be brought about in a variety of polymers.[29] These include polymers such as polypropylene and polycarbonates which do not normally crosslink via radiation or do so with very low efficiencies. This has been accomplished via the use of radiation in conjunction with polyfunctional monomers. This latter process has been extensively studied at RAI.[8]

It is our opinion that there are three alternate techniques for employing plastic memory to erect passive communications structures in space. These are:

Technique 1: A wire grid structure imbedded in (i.e., coated with) a plastic possessing memory. This would then be coated with a temperature-controlling coating that would allow the restoration process to occur in space and then disappear.

Technique 2: A wire grid structure coated with a plastic memory material which is also temperature-controlling and degradable in space.

Technique 3: A plastic memory grid material which is metallized. The metallized coating is in turn coated with a temperature-controlling degradable coating.

One should note that the end result, after restoration is complete and the degradable polymer has disappeared, is a wire structure for Technique 2, a wire structure imbedded in a plastic for Technique 1 and a metallized plastic structure for Technique 3.

At first glance it would seem that the second technique is the simplest one. It involves only one polymeric material and no bonding problems. However, the considerations necessary to stronly advocate one of these techniques over the others are not clear at this time. We, therefore, suggest that the feasibility of all three techniques be considered for future study.

It is suggested that future work involve the

a. development of a space degradable polymer,

b. development of a space degradable polymer possessing memory,

c. study of the precise extent of restoration,

d. space rigidization of erected structures.

7.1 Space Degradable Polymer

A space degradable material is necessary for using plastic memory to erect structures in space via the techniques above. This would contain the temperature-controlling additives (which possess the proper α/ϵ) in order to allow the restoration process to take place. After restoration is complete, this coating would be required to degrade and vaporize away.

Various approaches are possible to obtain a space degradable polymer. The most obvious is to employ a polymer of the degrading type such as polymethacrylate. The degradation could be speeded up by formulating the polymer with appreciable amount of a free radical initiator or UV sensitizer. Preliminary evidence indicates that this is a feasible approach and it is proposed to study it in detail.[29] Commercially available materials and other experimental materials should be investigated.

7.2 Space Degradable Polymer Possessing Memory

A space degradable polymer possessing memory would be necessary in order to employ Technique 2, described above for space erectable structures. The polymers to be investigated would be of the degrading type discussed in 7.1 above. Such polymers, because of their chemical structure, cannot be crosslinked by radiation... instead they degrade. However, as mentioned earlier, RAI has been able to radiation-crosslink such materials via the use of polyfunctional monomers.

It is suggested that one study the inducing of memory into polymers of the degrading type via the use of radiation in conjunction with polyfunctional monomers. The effect of various parameters such as deformation and restoration conditions, radiation dose, etc. on the degree of restoration and restoring force should be determined. Alternately, available materials which are crosslinked via non-radiation techniques and which exhibit memory and are space degrading should be investigated.

7.3 Precise Degree of Restoration

Our present work showed that the degree of restoration shown by polyethylene and its copolymers is 99+%. However, our test method was not precise enough to determine if the degree of restoration is 99.0% or 99.9% or 99.99%. It is suggested that the exact degree of restoration be determined by a study of the optical properties of metallized plastics.

This could be done by directing a thin cylindrical shell (tube) of collimated light toward the outer surface of a restored sphere either along a radius or at a known angle to the radius at the center of the area at which the light beam meets the surface of the sphere. The precise shape and size of the reflected beam would then be observed on a screen placed at a proper distance and altitude with respect to the sphere. This would be compared to the shape and size of the corresponding beam when reflected from a perfect sphere.

7.4 Rigidization

Although rigidization is not of importance for memory erection of Echo or Rebound-type structures in space, it would be required for other structures such as antennas, switches, etc. This would probably require the rigidization of the structures in space after erection. Plastics are available which have the high rigidity but their restoration temperatures are probably too high to be readily attained. High restoration temperatures are undesirable because they are difficult to attain and/or such temperatures would be detrimental to apparatus, instruments, etc. on the space structure. Although space rigidization has been studied,[30] its applicability to the memory effect is required. It is therefore recommended that the rigidization of structures erected via the memory effect be studied. Emphasis should be placed on the rigidization of restored structures made of polymers with low restoration temperatures. This would consist of studying the rigidization of those polymers studied under the subject contract (and also other low T_m polymers if desirable). Techniques of space rigidization recommended for consideration include the infrared curing of epoxy resin, the ultraviolet curing of unsaturated polyesters, the thermal activation of an isocyanate prepolymer to give a foam and the curing of melamine or phenolic resins by space activated catalysts. Encapsulation techniques should also be considered.

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