Memory Effects in Irradiated Polyethylene*

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Synopsis

The memory of irradiated polyethylene has been studied with emphasis on the magnitude of the restoration force exerted by the deformed polymer during the process of restoration to the nonstressed state and on the degree of completeness with which restoration occurs. The particular form of the memory effect studied has involved the deformation of the heated polymer followed by "locking-in" of the memory via cooling. Subsequent heating restores the deformed specimen to the undeformed state. The memory effect has been studied under both nontransparency (NT) and transparency (T) deformation conditions. The effects of parameters such as the polymer properties (T_m, density, molecular weight), radiation dose, and deformation and restoration conditions on the degree of restoration and restoration force have been investigated. The results of this study may be summarized as follows. Restoration temperatures equal to or above the crystalline melting point (T_m) of the polymer are required in order to obtain complete restoration. The restoration temperature increases with increasing polymer crystalline melting point. The degree of restoration increases with increasing restoration temperature for NT deformed specimens. T deformed specimens do not begin to restore until the temperature approaches the T_m of the polymer. The restoring force increases with decreasing deformation temperature. NT deformation results in larger restoring forces and faster restoration relative to T deformation. The restoring force increases with increasing radiation dose for both T and NT deformations, the effect being greater for NT deformation. Radiation dose, however, above a minimum value does not affect the degree of restoration. The restoring force increases with increasing polymer initial molecular weight for T deformation.

INTRODUCTION

The memory of irradiated polyethylene has been briefly referred to in the literature.[1-3] At ambient temperatures, it is similar to the unirradiated polymer; however, above its normal crystalline melting point (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 will be followed by recovery or relaxation.

Two different types of memory are present in irradiated polyethylene. One is the memory attributable to disrupted crystalline regions and is present in both unirradiated and irradiated polyethylene. The other is the

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memory attributable to disrupted crosslinked regions and is present only in crosslinked polyethylene. This paper presents the results of a study of the memory effects in irradiated polyethylene. The work has involved a study of the effects of various parameters (polyethylene properties, radiation dose, and deformation and restoration conditions) on (1) the degree of completeness with which restoration occurs and (2) the magnitude of the restoration forces exerted by the deformed polymer during the process of restoration to the nonstressed state.

EXPERIMENTAL

Materials

The properties of the various polyethylene homopolymers and ethylene–butene copolymers studied are listed in Table I. All of the polymers except Alathon 15 were studied in the form of 0.15 cm. thick molded sheets; Alathon 15 was studied as 0.15 cm. thick extruded tape.

TABLE I
Polyethylene Grades Evaluated for Memory Study[a]

Grade[b]	Density, g./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 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[c]	0.950	131–132	7.6	130	2.5
Grex 50-050[c]	0.950	131–132	6–7	70–80	5.0
Hi-Fax 1901	0.939	129–131	—	2000	ca. 0
Marlex 5003[c]	0.950	124	9.3–11	188–200	0.3
Marlex 6002	0.960	127	14.6	165	0.2

[a] All data supplied by the manufacturers of materials.

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

[c] These grades contain small amounts of butene-1 as copolymer to aid stress crack resistance. The Grex materials contain 2.5–3% and the Marlex 5% butene-1.

Irradiations

All irradiations except the low dose (4.3 Mrad) irradiations were performed with the use of a 1.5 M.e.v. High Voltage Engineering Corporation Model GS Van de Graaff electron accelerator. Irradiations were performed in air by placing the samples on Dry Ice (to prevent excessive heating) on trays which, in turn, sat on a moving belt that passed back and forth under the electron beam. The doses delivered to the samples were compensated for the secondary ionization effect 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 with γ-irradiation from a Co^{60} source.

Experimental Procedures

Polymer specimens (1 cm. wide and 7 cm. long) were thermally equilibrated at the desired deformation temperature in a silicone oil bath, deformed by folding with a pair of forceps and then quenched at 15°C. to "lock in" the memory. The point of deformation was always 2 cm. from one end of the sample. The deformation angle was defined as the number of degrees through which the specimen had been deformed. The specimens in this study were bent to a deformation angle of 180°. The deformed specimens were bent so as to have a sharp radius of curvature, the diameter at the inside of the apex being equal to or less than the specimen's thickness.

Degree of Restoration. Deformed specimens were placed in a silicon oil (d = 0.96 g./cc.) bath maintained at the desired restoration temperature. As restoration occurred, the decrease from an initial deformation angle of 180° was observed visually with a protractor. All experiments were performed at least in duplicate. The precision of degree of restoration measurements was ±1°. Complete restoration was defined as a return of the deformed specimen to a deformation angle of zero degrees.

Restoring Moment. This measurement involved the moving of a mass by the deformed specimen as it restored. The masses, consisting of flat lead strips, were of the same length and width as the upper part of the deformed specimen (i.e., 1 cm. × 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 constituted 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 plus lead mass were 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 Figure 1.

Experiments were continued until the maximum mass that could be moved was obtained. The experimental values of maximum mass moved and minimum mass not moved were obtained to within 5–10% of each other. The average of the maximum mass moved and the minimum mass not moved was defined as the restored mass. Multiplication of this value by the distance of the center of the mass to the apex of the deformed specimen (i.e., the mass–apex distance) yielded the restoring moment. All experiments were performed at least in duplicate. The precision of restoring moment measurements was ±10–15%.

Standard Conditions. The temperature at which the specimen is deformed was defined as the deformation temperature. The development of transparency in irradiated polyethylene[4] represented a convenient point for classifying the type of deformation performed. When the test specimen was maintained at a deformation temperature above the T_m of the unirradiated polymer and became transparent, the process was called a transparency or T deformation. When the specimen was maintained
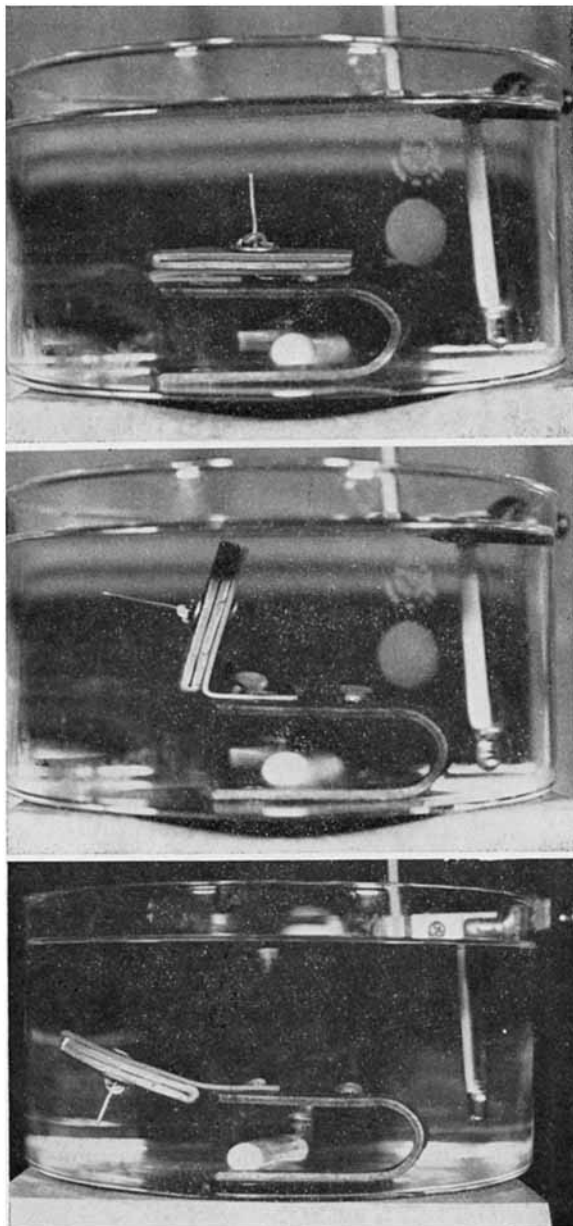
Fig. 1. Experimental setup (holder, deformed sample, and lead weight) for measurement of restoring moment.

at deformation temperatures below the polymer T_m and remained opaque, the process was called a nontransparency or NT deformation.   It was found desirable to adopt and define two sets of standard experimental conditions: one for T deformations and the other for NT.   These are listed in Table II.

TABLE II

Polyethylene molded sheets	Grex 50-050
Sample dimensions	
Length, cm.	7
Width, cm.	1
Thickness, cm.	0.15
Mass–apex distance, cm.	2.5
Radiation dose, Mrad	61
Deformation	
NT	80°C./hr.
T	140°C./5 min.
Deformation angle	180°
Sharp radius of curvature	
Deformation quench, °C.	15
Restoration, °C.	140

The T and NT standard conditions differed only in their respective deformation temperatures. Unless otherwise stated, these standard conditions were employed in all experiments. Departures from these specific conditions were made only when one of the parameters was the variable under study.

Experimental Limitations. The measurement of the deformation angle for restorations in which transparency did not occur was relatively simple since the specimen remained rigid during restoration. However, when restoration was carried out such that transparency developed, the specimen was no longer rigid upon restoration and the angle measurement was complicated. 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 then observing its deformation angle. This value was always observed to be zero degrees, i.e., the sample had restored to its original flat shape once transparency occurred. As will become evident from the experimental results, restoration during which transparency occurs always results in complete restoration.

The extent of rigid-body behavior under T restoration conditions was also noted by a series of experiments in which the restoring moment was observed to be the same to within ±25% for various mass–apex distances. This departure from rigid-body behavior was not considered excessive for the purposes of our study, since the main interest was not in the absolute values of the moments but rather in the relative dependence of the restoring moment on the various experimental parameters under study. The restoring moment data at the standard mass–apex distance of 2.5 cm. was found to be precise to within ±10–15%.

The calculated moments did not include the contribution due to the restoring specimen lifting itself. This contribution was very small, the specimen portion weighing less than 1 g., and was a constant for all our experiments. The moments were also not corrected for the work performed by

the restoring specimen in overcoming the viscous drag of the bath liquid on the moving specimen leg and affixed weights. Rough calculations indicated that this was a negligible contribution to the restoring moment.

RESULTS

Degree of Restoration

Deformation Conditions. The deformation conditions were found to have a significant effect on the restoration behavior but no effect on the degree of restoration. Complete restoration occurred under a variety of deformation conditions if the restoration temperature was above the crystalline melting point of the polymer.

The lower the deformation temperature, the more rapidly did restoration begin. Thus, specimens deformed at 40°C. begin to restore almost immediately. As the deformation temperature was increased, the onset of restoration was delayed. When deformation was performed under transparency conditions, the time interval between immersion in the hot restoration environment and the beginning of restoration was greatest (ca. 3 min.).

Unirradiated and irradiated polyethylene behaved very similarly at deformation (and restoration) temperatures below T_m. Unirradiated polyethylene could be deformed at temperatures below its T_m; upon being placed in the restoration environment, these specimens began to restore. However, restoration was incomplete, and melting of test specimens occurred as they approached the polymer T_m. Also, T deformations could not be performed on unirradiated polyethylene.

Restoration Conditions. The restoration temperature was found to be of profound importance in controlling the degree of restoration of NT deformed polyethylene. Restoration began to occur over the entire testing
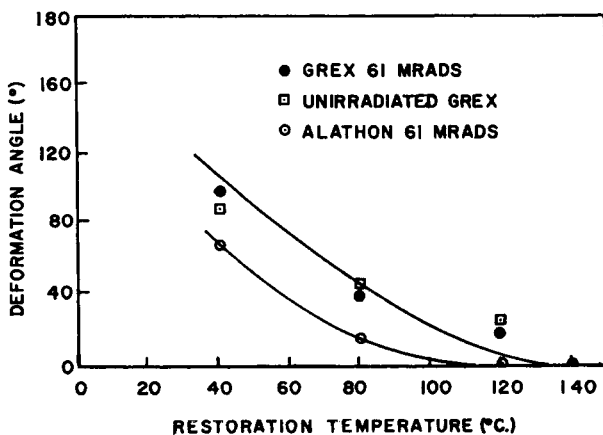

Fig. 2. Effect of restoration temperature on degree of restoration (NT deformation).

temperature range.   However, the degree of completion was greater as the restoration temperature was increased.   For restoration to be complete, the polyethylene must be heated to transparency (i.e., at or above its T_m). For high density polyethylene, this temperature was ca. 135°C.; for low density, ca. 110°C.   These results are shown in Figure 2 for Grex 50-050 ($d = 0.95$ g./cc.) and Alathon 15 ($d = 0.916$ g./cc.).   It should be noted that unirradiated polyethylene behaves very similarly to irradiated polyethylene except at T_m.

T deformed Grex 50–050 was studied in a similar manner.   It was observed that restoration did not occur at the lower restoration temperatures. As the restoration temperature was 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.

Radiation Dose.   Radiation dose did not affect the degree of restoration above the minimal dose of ca. 4.3–12 Mrad for a polyethylene of $\bar{M}_w$ of at least 70,000.   Thus, for such polyethylenes 12 Mrad was sufficient dosage for complete restoration of both T and NT deformed specimens while 4.3 Mrad was insufficient.   However, when the polyethylene $\bar{M}_w$ was 2500 (Epolene E-10), even 61 Mrad was insufficient to allow restoration.

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.   Thus, standard NT deformed Grex 50-050 specimens could readily be prevented from restoring while in the restoration bath 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 NT deformed specimen, while held in the deformed state, underwent crystalline melting and its behavior then became exactly like the T deformed specimen.   The restoring force under these conditions was equivalent to that observed under T deformation.

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 restora-

tion, placed in the restoration bath for various time intervals, the clamps then removed and the restoration behavior of the deformed specimens 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 restoration bath for $4^1/_2$ hr. subsequently restored to a deformation angle of 10° while 1-week specimens restored to a deformation angle of 90°.

Restoring Moment

Deformation Conditions.   It was observed that the restoring moment was highly dependent upon the deformation conditions.   If the deformation temperature was low, the restoring moment was relatively high.   As the deformation temperature was increased, the restoring moment decreased. When the deformation temperature was high enough so that transparency occurred, the restoring moment was at a minimum.   These results are shown graphically in Figure 3 for Grex 50-050.   The results indicate not only a decrease in restoring moment with increasing deformation temperature, but also that the greatest decrease occurs as the T_m is approached.
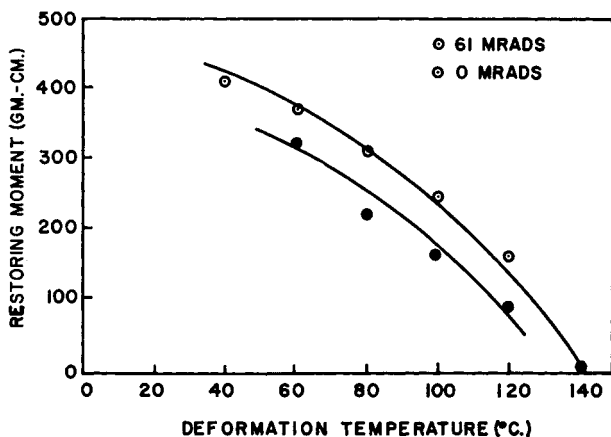

Fig. 3. Effect of deformation temperature on restoring moment of Grex 50-050.

Unirradiated polyethylene could also be tested under standard NT deformation conditions.   The results (Fig. 3) showed that restoration with the manifestation of relatively large moments could occur.   However, for each deformation temperature, the restoring moment was less than for the 61 Mrad polyethylene.

Restoration Conditions.   The restoration temperature was found to have no effect on the restoration moment if restoration occurred.   The restoring moment was not dependent on whether complete restoration occurred but only on the occurrence of restoration.
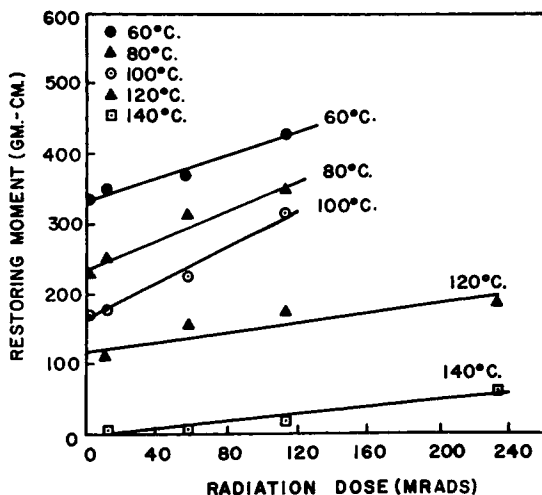
Fig. 4. Effect of radiation dose on restoring moment of Grex 50-050 at various deformation temperatures.
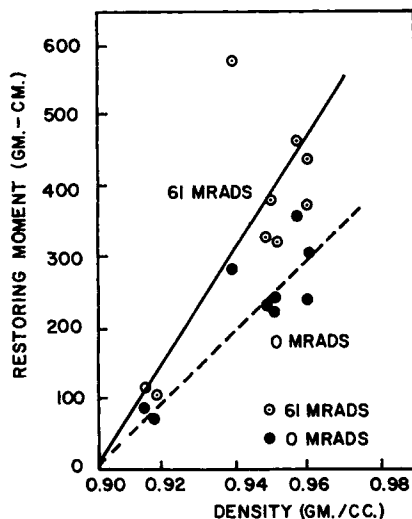

Fig. 5. Effect of density on restoring moment.

The restoring moment of standard NT deformed specimens was 315 g.-cm. at 140°C. and was 300 g.-cm. at 80°C. This difference is within experimental error. It was concluded, therefore, that no discernible difference in restoring force occurred at the lower restoration temperature. The restoration temperature effect on restoring moment after standard T deformation conditions was not considered for study since restoration here does not occur unless the restoration temperature is in the vicinity of the normal polymer T_m.

Radiation Dose.   The effect of radiation dose on the restoring moment of Grex 50-050 was studied at various deformation temperatures over the dose range 12–245 Mrad.   Higher doses were not tested because of the brittleness of specimens at the 245 Mrad dose.   (Cracking occurred with the 60–100°C. deformed specimens when the dose was 245 Mrad.)   The results (Fig. 4) showed an increasing restoring moment with radiation dose for both T and NT deformation with the effect being greater for NT deformation.   Similar results were observed with Alathon 15 low density polyethylene.

Crystallinity.   The effect of polyethylene crystallinity on the restoring moment was determined by employing nine different grades of polyethylene with varying density and crystalline melting point.   Along with 61 Mrad
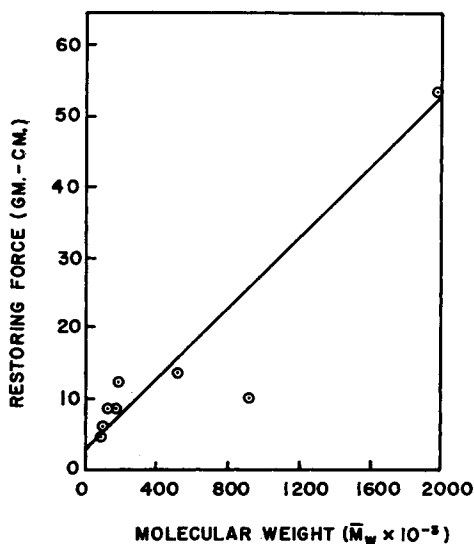

Fig. 6. Effect of molecular weight on restoring moment.

polymer tested under standard NT conditions, unirradiated controls were also run.   The results (Fig. 5) showed the restoring moment to increase with increasing crystalline melting point and density (both of which are measures of crystallinity).

It should be noted that the experimental point for Hi-Fax 1901 in Figure 5 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 moment would be crystallinity; however, such data was not generally available.   The other deviations from the straight line plot in Figure 5 may be explained by assuming that initial molecular weight or crosslink density is a contributing factor to the restoring moment.

Initial Molecular Weight. The effect of polyethylene initial molecular weight (i.e., $\bar{M}_n$ or $\bar{M}_w$ prior to irradiation) on restoring moment was investigated by studying nine different polyethylene grades under T deformation conditions. Since T deformation causes complete crystalline melting prior to deformation, this experimental approach meant that polyethylene crystallinity did not play an appreciable role in the restoring moment, and the latter would be related solely to the crosslinked polymer network. The results (Fig. 6) of these tests indicated an increasing restoring moment with increasing dose.

DISCUSSION

On the basis of all the available data and information, it is felt that a comprehensive mechanism can be proposed to explain the memory of irradiated polyethylene. We do not wish, here, to discuss the exact nature of crystalline polyethylene but will discuss the memory effects in terms of the disruptions and destabilizations of polymer structure which occur during deformation and of the subsequent relieving of these during restoration.

Polyethylene can be thought of as consisting of crystalline and non-crystalline regions.[5,6] 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 crosslinks between chains. (Irradiation of polyethylene also results in other changes such as in the nature and concentration of unsaturation;[3] however, these are not thought to affect the memory phenomenon under our experimental conditions.)

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. The memory of the deformed polymer is due to its attempted restabilization. We wish here to define the memory due to disrupted crystalline regions as crystalline memory and that due to disrupted crosslinked regions as crosslink memory. The memory observed in NT deformed polyethylene is caused by a combination of crystalline and crosslink memories; that observed in T deformed polyethylene is due only to crosslink memory. It should be obvious that crystalline memory is inherent in polyethylene (and other polymers) and is not at all dependent on crosslinking; but only crosslinked polyethylene (and other polymers) possesses crosslink memory.

When irradiated polyethylene is deformed at NT temperatures, the deformed specimens begins to restore immediately at ambient temperatures (25°C.). In other words, NT deformations cannot be locked in; restoration begins immediately. 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 lack of locking in of memory are based on the melting and recrystallization of various polyethylene regions during the deformation and quenching process.

Deformation of polyethylene at temperatures above the melting point of some crystalline regions 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 prior to recrystallization during the quenching part of the deformation process. Thus, the deformed specimen consists of a highly dynamic situation. The crystalline/crosslink 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 (at higher deformation temperatures), the forces of stabilization increase and move in the direction of overcoming the forces of restoration. In actual practice we have observed that the crystalline 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 crystalline memory restoring forces to be much larger than the crosslink memory restoring forces. It should be mentioned that as the deformation temperature increases for NT deformation, 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 crystalline and crosslink memory. As the deformation temperature is increased, the amount of crystalline 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 deformation. 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 crystalline memory. The memory of such a T deformed specimen

is solely due to crosslink 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 crosslink 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 crystalline 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 increasing radiation dose. This has been, of course, attributed to the fact that crosslinking results in crosslink memory and that the extent of crosslink 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 indicates that under T deformation conditions the crosslinked polymer network is sufficiently mobile that some of the crosslinks may establish new stable configurations and thus not be a source of instability in the deformed specimen. The mobility of the polymer crosslinks is also responsible for the observed loss of memory of T deformed specimens which are heated above the T_m while being prevented from restoring.

The increase in restoring moment with increased polymer density under NT deformation conditions is explainable on the basis of the amount of crystalline melting which occurs during the deformation process.   At the NT deformation temperature of 80°C., greater amounts of crystalline melting occur for the polymers possessing low crystalline melting points and these possess, in the deformed state, smaller amounts of deformed crystalline regions than the high density polyethylenes.

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.   The negative deviation of the restoring moment of Alathon 14 from the line in Figure 6 may be due to partial stabilization of the crosslinks (during deformation) due to their mobility.   Since Alathon 14 has the lowest T_m of the polymers studied, its crosslinks, relative to those of the other polymers, would have the greatest opportunity during the T deformation process to establish a stable configuration.

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Résumé

On a étudié la mémoire du polyéthylène irradié. On s'est particulièrement intéressé à la grandeur de la force de recouvrement de l'état sans tension et au degré de perfection du recouvrement. La forme particulière du phénomène à mémoire étudié comprend la déformation du polymère chauffé suivie du blocage de la mémoire par refroidissement. Un chauffage ultérieur rend à l'échantillon déformé sa forme primitive. On a étudié l'effet de mémoire dans des conditions où le polymère garde sa transparence (T) ou perd sa transparence (NT). On a étudié l'effet des propriétés des polymères (T_m, densité, poids moléculaire) de la dose de radiation et des conditions de déformation et de restoration sur la force et le degré de recouvrement. On peut résumer les résultats de cette étude comme suit: Des températures de recouvrement égales ou supérieures au point de fusion cristallin (T_m) du polymère sont nécessaires pour que le recouvrement soit complet. La température à laquelle se fait le recouvrement augmente avec l'élévation du point de fusion cristallin. Le degré de recouvrement des échantillons, qui ne restent pas transparents après déformation, augmente avec l'élévation de la température à laquelle se fait le recouvrement. Le processus de recouvrement des échantillons restés transparents après déformation ne commence pas avant que la température ne s'approche de la température de fusion du polymère. La force de recouvrement diminue avec l'abaissement de la température de la déformation. Les déformations (NT) produisent des forces de recouvrement et des vitesses de recouvrement supérieures de déformation (T). La force de recouvrement augmente si l'on augmente la dose de radiation dans le cas de déformation T et NT. L'effet est plus marqué dans le cas des déformation NT. Cependant la dose de radiation n'affecte pas audessus d'une valeur minimum limite, le degré de recouvrement. La force de recouvrement augmente avec l'élévation du degré de polymérisation initial pour des déformation de type T.

Zusammenfassung

Das Erinnerungsvermögen von vestrahltem Polyäthylen wurde besonders in Hinblick auf die Grösse der vom verformten Polymeren während des Prozesses der Rückbildung des unbeanspruchten Zustandes ausgeübten Rückbildungskraft und auf die Vollständigkeit der Rückbildung untersucht. Speziell untersucht wurde das Erinnerungsvermögen bei Verformung des erhitzten Polymeren mit darauffolgender "Sperrung" des Erinnerungsvermögens durch Abkühlung. Neuerliches Erhitzen bringt die verformte

Probe wieder in den unverformten Zustand. Das Erinnerungsvermögen wurde unter den Bedingungen einer Verformung im Nichttransparenz-(NT)- und Transparenz-(T)-Zustand untersucht. Der Einfluss der Polymereigenschaften (T_m, Dichte, Molekulargewicht), der Bestrahlungsdosis sowie der Verformungs- und Rückbildungsbedingungen auf Rückbildungsgrad und -kraft wurden untersucht. Die Ergebnisse dieser Arbeit können wie folgt zusammengefasst werden: Rückbildungstemperaturen gleich oder oberhalb des Kristallitschmelzpunktes (T_m) des Polymeren sind zu einer vollständigen Rückbildung erforderlich. Die Rückbildungstemperatur steigt mit Zunahme des Polymer-Kristallitschmelzpunktes an. Der Rückbildungsgrad nimmt bei NT-verformten Proben mit wachsender Rückbildungstemperatur zu. Bei T-verformten Proben beginnt Rückbildung erst bei Annäherung der Temperatur an T_m des Polymeren. Die Rückbildungskraft steigt mit abnehmender Verformungstemperatur an. NT-Verformung führt im Verhältnis zur T-Verformung zu grösseren Rückbildungskräften und zu rascherer Rückbildung. Die Rückbildungskraft nimmt bei T- und NT-Verformung mit steigender Bestrahlungsdosis zu, wobei der Effekt bei der NT-Verformung grösser ist. Hingegen hat die Bestrahlungsdosis oberhalb eines gewissen Mindestwertes keinen Einfluss auf den Rückbildungsgrad. Die Rückbildungskraft nimmt bei T-Verformung mit steigenden Anfangsmolekulargewicht des Polymeren zu.