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# Characterization of Polymer Films Retrieved from NASA's Long Duration Exposure Facility

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**The results of chemical and physical tests of thin-film polyethylene exposed to the low-Earth-orbit environment are presented. These materials were placed in orbit aboard NASA's Long Duration Exposure Facility. The primary objective of the research is to examine the effect of atomic oxygen in the presence of ultraviolet radiation on materials used in the design of flight systems. The location of these materials on the satellite minimized direct impact by atomic oxygen, thus providing an opportunity to study the effects of the low-Earth-orbit environment on polymer materials in the absence of direct impact atomic oxygen. The chemical, morphological, and mechanical changes for polyethylene specimens are reviewed.**

## Nomenclature

$a_T$ = temperature-dependent shift factor
$E^*$ = dynamic modulus
$E'$ = storage modulus
$E''$ = loss modulus
$M$ = molecular weight distribution
$T$ = temperature
$t$ = time
$\Delta H_f$ = heat of fusion (true)
$\Delta H_f^*$ = heat of fusion (measured)
$\delta$ = material damping
$\varepsilon$ = strain
$\varepsilon_o$ = magnitude of oscillatory strain
$\eta$ = intrinsic viscosity
$\lambda$ = branching frequency
$\mu$ = branching index
$\sigma$ = stress
$\sigma_o$ = magnitude of oscillatory stress
$\chi$ = crystallinity
$\omega$ = frequency

## Introduction

RECENT investigations have suggested that the exposure of polymers to the low-Earth-orbit (LEO) environment may result in significant degradation caused by atomic oxygen attack in the presence of ultraviolet radiation. LEO is the region between 200 and 500 km above the Earth and has an atmosphere that consists predominantly of atomic oxygen.[1] Spacecraft in this region travel at a rate of 8 km/s, which has the effect of providing the atomic oxygen with a translational energy of approximately 5 eV as it strikes the leading surfaces. Under these conditions, mass loss occurs, and the properties of many polymers are degraded because of atomic oxygen in the presence of ultraviolet radiation. The increasing importance of polymers in orbiting spacecraft has required an understanding of how, and to what extent, the properties of polymers are affected by this type of environment. As a result, suitable polymers can be identified or developed for LEO applications.

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This paper presents the results of experimental tests and analyses performed on thin-film polymers retrieved from the Long Duration Exposure Facility (LDEF) satellite. LDEF was developed by NASA to accommodate several independent self-contained experiments. The experiments were positioned on trays mounted on the exterior of the structure.[2] LDEF had no active control systems; rather, LDEF maintained a stable position using a gravity-gradient design. The mechanics of the orbit were such that one end of LDEF faced the Earth and one specific side was aligned with the orbital velocity vector. Initially, LDEF was placed in LEO at a nominal altitude of 476 km. The orbit decayed to a nominal altitude of 333 km at the time LDEF was recovered.[3] LDEF was placed in LEO in April of 1984, and it was scheduled to be recovered after 10 months on orbit; however, recovery did not occur until January 1990.[4,5] The extended duration of the LDEF mission significantly enhanced our studies to characterize the properties of the exposed specimens.

An experiment consisting of polymer materials was developed by Texas A&M University. The LDEF designation for this experiment was S1006.[6] The materials included polyethylene, polyester, and nylon films in addition to fiber-reinforced polymer films and polymer lines. The experiment was positioned on LDEF in such a way that the plane of the specimens coincided with the plane of the orbit; thus, the normal to the surface of each specimen was perpendicular to the impact direction of the atomic oxygen. Consequently, abrasion from atomic oxygen was minimized. Furthermore, the specimens were shielded because the mounting tray for the experiment was recessed within the supporting structure.

The specimens were exposed to a moderate fluence of atomic oxygen ($4.93 \times 10^{19}$ atoms/cm$^2$) as compared with other experiment positions.[3,7–9] The maximum atomic oxygen fluence ($8.33 \times 10^{21}$ atoms/cm$^2$) was received by experiments along the leading surface of LDEF. The minimum fluence of atomic oxygen ($3.34 \times 10^3$ atoms/cm$^2$) was received by experiments along the trailing surface of LDEF. It should be noted that polymer films thicker by an order of magnitude were eroded from the leading surface because of the fluence.

The specimens were exposed to the smallest amount of direct sunlight, as compared with most other experiment positions.[8,9,10] Except for the experiments located on the Earth-facing end of LDEF, these specimens were exposed to the fewest equivalent sun hours (6500). The maximum number of equivalent sun hours (14,500) was received by experiments located at the space end of LDEF. Temperatures for the specimens were not measured directly; however, the temperatures for the support structure were predicted to range between −21 and 51°C.

Research objectives include a comprehensive program of tests and analyses to characterize the properties of the exposed specimens. The investigations include differential scanning calorimetry, size-exclusion chromatography, Fourier transform infrared spectroscopy, dynamic mechanical analysis, and scan-

ning electron microscopy. Results are presented for polyethylene specimens.

## Materials

The experiment consists of 38 thin-film polymer specimens and 24 fibrous cord specimens.[6] Two sets of control specimens are available for comparative studies. The thickness of the polymer specimens ranged from 8.9 to 46.0 $\mu$m. The specimens were primarily polyethylenes and polyesters. Several specimens are reinforced with nylon, Kevlar®, or polyester fibers. Herein, the investigations of two materials are reported. The first material is low-density polyethylene (LDPE). The nominal specimen thickness is 25.4 $\mu$m. The second material, referred to as HDPE/LLDPE, is a blend of high-density polyethylene (HDPE) and linear-low-density polyethylene (LLDPE). The nominal specimen thickness is 8.9 $\mu$m. Each exposed specimen is 150 mm long and 25.4 mm wide. The materials are produced using a blown-film process that induces direction-dependent behavior; thus, specimens in the machine direction and transverse direction are included.

## Experimental and Analytical Procedures

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on the specimens using a DuPont-1090 controller with a DuPont-910 cell. The specimens were tested according to ASTM D-3418 specifications. These tests measured differences in percent crystallinity between specimens. DSC scans were conducted in the following sequence: heat at 10°C per min to 190°C, maintain a constant temperature for 10 min, cool at 10°C per min to 50°C, and reheat at 10°C per min. This procedure provided the initial melting temperature and heat of fusion. Crystallization and second melting temperatures were determined, in addition to the associated specific heats.

The percent crystallinity is found as

$$\chi = \left(\Delta H_f^* / \Delta H_f\right) \times 100 \tag{1}$$

where $\Delta H_f^*$ is measured from the specimen, and $\Delta H_f$ is measured from an equivalent mass of a perfect crystalline polyethylene. The heat of fusion of crystalline dotriacontane is used as the true heat of fusion for a completely crystalline polyethylene.[11]

### Size-Exclusion Chromatography

Size-exclusion chromatography (SEC) was conducted using a Waters Associates 150C ALC/GPC with a Viscotek 150R differential viscometer retrofit. Orthodichlorobenzene (ODCB) at 135°C with a flow rate of 1.2 ml/min was employed as the solvent. This particular SEC uses 250 ml injections and column sets of $10^3$, $10^4$, $10^5$, and $10^6$ mm. Control and exposed specimens were dissolved and tested as a 0.125% solution ($w/v$). Calibration was done using a linear polyethylene reference (NIST standard number 1474). The apparent molecular weight distribution (MWD) and intrinsic viscosity were obtained. In addition, branching frequency and actual MWD were determined.

The branching frequency, defined as the number of branched units in a molecule divided by the molecular weight,[12] is determined by application of the theory of Zimm and Stockmayer. This theory relates $\mu$ to the product of $\lambda$ and $M$. Initially, $\lambda$ is assumed constant, and the universal calibration for the SEC is used to convert the chromatogram into a distribution of $\eta M$. The molecular weight values are converted into corresponding values of $\lambda M$, from which $\mu$, $\eta$, and $\eta M$ values are determined. The assumed value of $\lambda$ is adjusted in an iterative manner such that the calculated value of $\eta$ is equal to the measured value of $\eta$. Consequently, $\lambda$ and $M$ are determined.

### Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra were collected using direct transmission and attenuated total reflectance (ATR) configurations. A Nicolet 520 was used for the direct transmission spectra and a Nicolet 60SXB was used for the ATR spectra.

### Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed to describe the viscoelastic characteristics of the specimens. Experimental measurements were accomplished through the use of a Rheometrics Solids Analyzer II. Tests were conducted through a range of frequencies ($0.1 \leq \omega \leq 100$ rad/s) and a range of temperatures ($-150 \leq T \leq 100$°C). Measurements were conducted at temperatures extending beyond the glassy region of the material.

In the DMA studies, forced response due to a oscillatory deformation input is measured. Material damping is the phase lag $\delta$ between the measured force response,

$$\sigma = \sigma_o e^{i(\omega t + \delta)} \tag{2}$$

and the oscillatory strain input,

$$\varepsilon = \varepsilon_o e^{i\omega t} \tag{3}$$

$E^*$ is derived from these measurements as

$$E^*(\omega, T) = \sigma/\varepsilon = (\sigma_o/\varepsilon_o)e^{i\delta} = |E|e^{i\delta} = E' + iE'' \tag{4}$$

where $E' = |E| \cos\delta$ and $E'' = |E| \sin\delta$.

The magnitude of the oscillatory strain input was selected to assure linear viscoelastic behavior, herein defined as the level in which the measured dynamic modulus is independent of the magnitude of the oscillatory strain. The specimens were preloaded to maintain tensile loads during the oscillatory tests.

The characterization is simplified by time–temperature correspondence principles.[13] If linear viscoelastic behavior exists, then the properties measured at one temperature and frequency are related through a temperature-dependent shift factor to the properties at another temperature and frequency, such that

$$E^*(T_1, \omega) = E^*(T_2, \omega a_T) \tag{5}$$

The shift factor $a_T$ is a measure of the temperature dependence for the relaxation process and is determined by the superposition of measurements at two distinct temperatures. The effect of a change in temperature is equivalent to shifting the mechanical response to a different range of frequencies. This strategy allows the superposition of measurements over a range of frequencies at a specific temperature with measurements at a second temperature. A master curve of the dynamic modulus as a function of frequency is formed for a reference temperature.

Traditional creep measurements require significant test time to characterize the viscoelastic properties adequately. However, the transformation of the modulus measured in the frequency domain to the modulus in the time domain provides rapid characterization. A method described by Ninomiya and Ferry[14] is used to determine the stress relaxation modulus

$$E(t) = E'(\omega) - 0.40[E'(0.4\omega)] + .014[E''(10\omega)]_{\omega=1/t} \tag{6}$$

where $\omega t = 1$.

### Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to produce micrographs of the surfaces of the films. SEM was conducted using a JEOL JSM-T330A electron microscope. The specimens were coated with 250 Å of gold-palladium and scanned with an accelerating voltage of 20 kV.

## Results and Discussion

### LDPE Specimens

DSC results are presented in Fig. 1. Initial and second melting temperatures for the control specimen are close to the second melt occurring at 107.3°C and with an endothermic transition of 106 J/g. On cooling, recrystallization occurs at 94.7°C with an exothermic heat of 111.0 J/g. The melting temperatures for the exposed LDPE are considerably depressed in comparison to the control LDPE. The initial and second melt temperatures are 101.6°C.

A permanent change in the molecular structure of the exposed LDPE occurs due to LEO exposure. This change is evidenced by

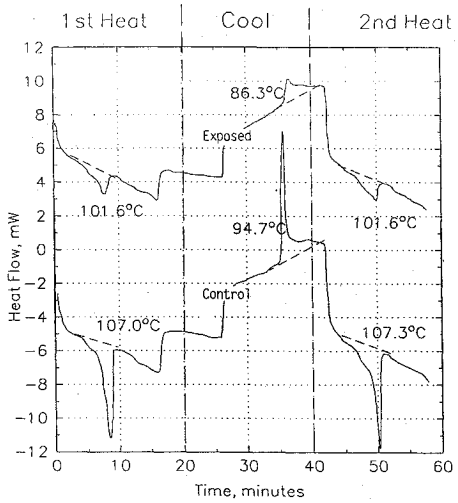


**Fig. 1 DSC thermogram for a heating, cooling, and second heating cycle for the exposed and control LDPE specimens.**

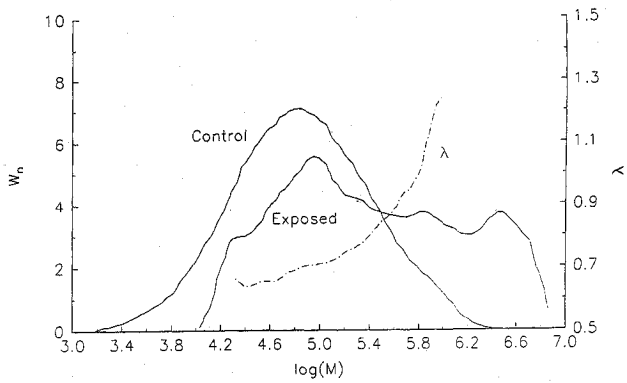


**Fig. 2 Molecular weight distribution for the control LDPE and the soluble portion of the exposed LDPE. The dependence of branching frequency (branches per 100 carbons) on the molecular weight of the exposed LDPE is presented.**

the decrease in the melting temperature as compared with the control LDPE. The melting temperature is consistent after repeated heatings, suggesting the existence of a cross-linked crystal structure. The corresponding heats of fusion for the exposed LDPE have decreased indicating a reduction in crystallinity and a possible decrease in lamella size. Recrystallization of the exposed LDPE occurred at 86.3°C with an endothermic enthalpy of 58.4 J/g. The enthalpy associated with the second melt was 64.4 J/g. The crystallinity percentage for the control LDPE was 39% and the crystallinity percentage for the exposed LDPE was 23.8%. The depression of the melting point and the decrease in crystallinity suggest that branching has occurred. Therefore, SEC measurements were used to determine branching frequency.

Figure 2 presents the molecular weight distribution for the control LDPE and the soluble portion of the exposed LDPE. Only 8% (by weight) of the exposed LDPE could be dissolved, which is a clear indication that cross-linking has occurred. The results show that the higher molecular weight molecules cross link to form an insoluble gel. The branching frequency for the control LDPE is also presented. These results show an increase in the branching frequency with an increase in the molecular weight for the exposed LDPE.

The presence of gel formation and branches brought about by exposure to LEO is evidenced by FTIR results. The FTIR data for two regions of interest are presented in Fig. 3. These measurements are associated with the 1470 $cm^{-1}$ band and the 730–720 $cm^{-1}$ band. The 730–720 $cm^{-1}$ band is associated with two chain structures. The 720 $cm^{-1}$ absorption band represents vibrations associated with aliphatic hydrocarbons; the 730 $cm^{-1}$ absorption band represents vibrations associated with methylene structures. The relative change in peak absorbance in this region suggests the presence of branches and/or cross-links in the structure. These same results

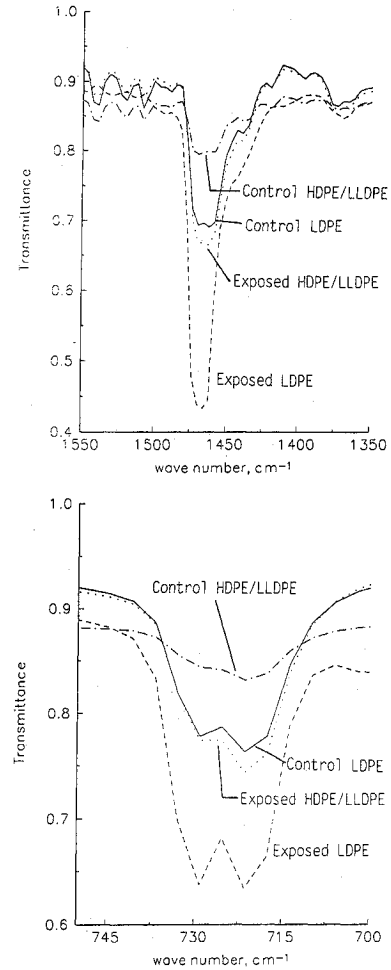


**Fig. 3 FTIR transmittance spectra for the exposed and control LDPE, and for the exposed and control HDPE/LLDPE. The 720–730 $cm^{-1}$ absorbtion band and 1470 $cm^{-1}$ absorbtion band are highlighted.**

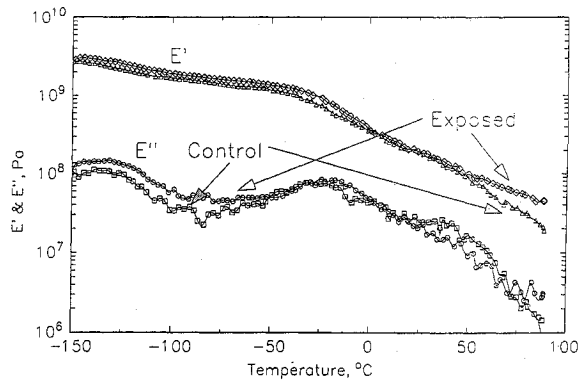


**Fig. 4 Storage, $E'$, and loss, $E''$, moduli for the LDPE (measured at a constant frequency of 1.6 hz).**

are evident in the 1470 $cm^{-1}$ band. The peak intensity and peak ratio (730 $cm^{-1}$/720 $cm^{-1}$) changes as the specimens are exposed to LEO, suggesting an increase in the amount of branching and cross-linking.

The changes in structure and crystallinity have a small effect on the mechanical properties of the LDPE. In Fig. 4, the dynamic modulus is presented for the specimens. Below −25°C, the LDPE is within the glassy region where localized motions dominate. As expected, cross-linking and branching have little effect on mechanical properties in this region. Above this temperature, an increase in the dynamic modulus is associated with increased cross-linking. Branching is expected to have little effect on the storage modulus but may increase the loss modulus because of the increased relaxations. The measurements indicate both cross-linking and branching have occurred. Cross-linking is evident by the increase in the

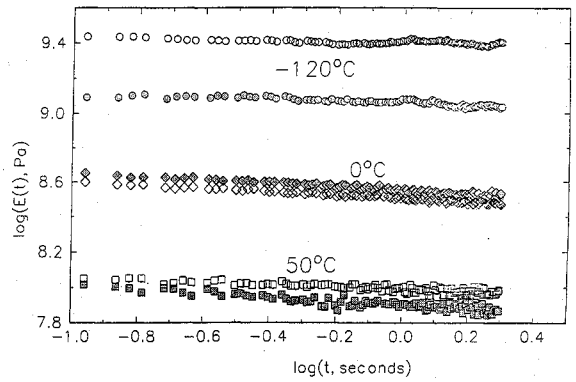


**Fig. 5 Relaxation modulus at three temperatures for the exposed and control LDPE.**

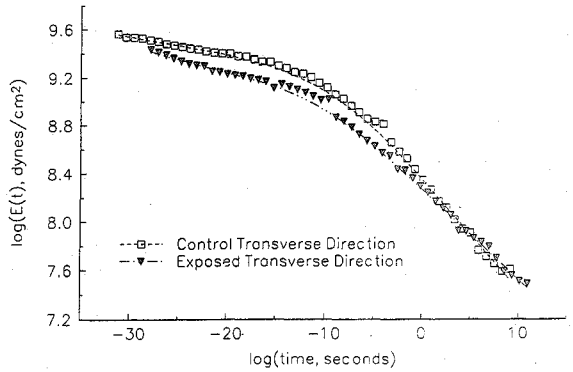


**Fig. 6 Relaxation modulus master curve for the LDPE (transverse direction).**

storage modulus at the higher temperatures. Branching is evident by the increase in the loss modulus for the same region. In general, the changes observed are small, which suggests that the distribution and size of crystalline structures may be more important than branching or cross-linking in these systems. This hypothesis is investigated further using light-scattering and x-ray scattering analysis.

The stress relaxation data presented in Fig. 5 supports the hypothesis that branching and cross-linking have little effect on the mechanical properties. At −120 and 50°C the relaxation modulus of the exposed LDPE is higher than the control LDPE, which suggests a cross-linking mechanism might be present. The fact that the relaxation curves parallel each other indicates no change in the relaxation mechanisms. At 0°C the modulus of the control LDPE is higher than that of the exposed LDPE. This temperature is within the glassy transition region; the measured change in modulus is a result of the difference in the glass transition profiles. Time–temperature superposition yields a master curve (Fig. 6) for the stress relaxation modulus. The reference temperature is 25°C. The results suggest an increase in modulus caused by LEO exposure.

### HDPE/LLDPE Specimens

DSC measurements for the HDPE/LLDPE specimens behave in a manner similar to the LDPE specimens. Consequently, only numerical results are presented but, as a reference, the DSC thermogram shown in Fig. 1 provides a similar profile. Melting occurs at 125°C, with an endothermic transition of 117.8 J/g. Recrystallization occurs after cooling at a temperature of 113.6°C with an exothermic heat of crystallization of 133 J/g. The thermogram indicates a significant depression in the melting point temperature of the exposed specimen. Essentially, there is no change in the melting temperature of the exposed specimen after reheating. The second melt occurs at 101.5°C, and the endothermic heat of fusion is 44.2 J/g. The crystallinity percentage of the control specimen is 46.2%, and the crystallinity percentage of the exposed specimen is 16.3%.

SEM micrographs aid in determining the effect of LEO exposure on the morphology and physical properties of the materials. Figure 7 presents SEM micrographs of the HDPE/LLDPE specimen. Notable is the presence of lamella on the surface of the control specimen. The micrograph of the exposed specimen does not

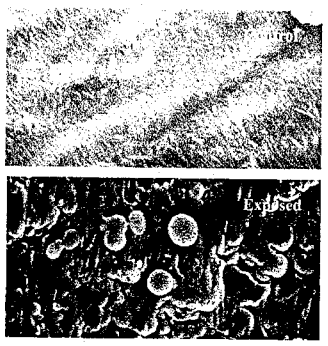


**Fig. 7 SEM micrograph for the control and exposed HDPE/LLDPE (recorded with a 10 deg tilt).**

show the "rug-like" surface typical of a polymer exposed to impact atomic oxygen. Rather, the micrograph shows a number of microscopic spheres on the surface of the exposed specimen. These spheres are formed by the solidification of molten polyethylene under microgravity conditions. The micrograph provides evidence that melting occurred on the polyethylene surface, suggesting that the estimated maximum temperature of 50°C was exceeded. Furthermore, the micrograph provides evidence that impact atomic oxygen was not significant at the location of the experiment because these spheres would have been eroded had exposure to impact atomic oxygen occurred.

The presence of branches brought about by exposure to LEO is evidenced by FTIR results. FTIR data for two regions of interest are presented in Fig. 3. These measurements are associated with the 730–720 $cm^{-1}$ band and the 1464 $cm^{-1}$ band. The relative change in peak absorbance suggests the presence of branches and cross links in the structure.

## Conclusions

The particular location of the experiment shielded the specimens from the direct impact of atomic oxygen. The materials were in a relatively benign environment and, as a consequence, the results provide insight into the possible changes to polymer materials exposed to diffuse atomic oxygen in the presence of ultraviolet radiation.

Measurements of reduced crystallinity, increased branching, and increased cross-link frequency suggest that chemical changes occurred simultaneously with thermal cycling. This observed behavior is supported by SEM micrographs of the specimens demonstrating melting. The exposed specimens show crystalline lamella in the process of melting. The kinetics of melting for these materials are on the same order of magnitude as the cross-linking process; if cross-linking occurred first then the spheres would not have been able to form.

Crystallinity and melting temperature decreased with a concurrent increase in both crosslinking and branching. The insoluble portion of the specimens found from SEC measurements is an indicator of the amount of cross-linking present. The measured viscoelastic properties suggest that the crystalline nature of the specimen contributes significantly to the overall mechanical properties. This observation is based on the fact that 92% (by weight) of the polymer chains were involved in cross-linking but only a slight change in the viscoelastic properties was observed. These results suggest that crystallinity dominates in the observed changes in mechanical properties.

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