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INFRARED ANALYSIS OF POLYETHYLENE WEAR
SPECIMENS USING ATTENUATED TOTAL
REFLECTION SPECTROSCOPY

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SUMMARY

Attenuated total reflection infrared spectroscopy (ATR) was used to analyze ultrahigh molecular weight polyethylene wear test specimens. Three different specimens were analyzed. One specimen had been gamma irradiated to a dose of 5.0 MRad, another to a dose of 2.5 MRad, and the final specimen was unirradiated. There was no conclusive evidence of chemical changes (i. e., unsaturation or oxidation) detected by ATR in the surface regions of any of the polyethylene samples. Therefore, it was concluded that the gamma irradiation sterilization procedure should not alter the boundary lubricating properties of the polyethylene with regard to adsorption of lubricant surface active species.

INTRODUCTION

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Ultrahigh molecular weight polyethylene (UHMWPE) is commonly used in total joint prostheses. This polymer possesses high wear resistance, chemical inertness, and is compatible with the body (ref. 1). However, the conventional sterilization technique of steam autoclaving cannot be used with polyethylene components because the deformation temperatures of the polymer are exceeded. Therefore, polyethylene components are normally sterilized with gamma irradiation (2.5 MRad dose) (ref. 2).

The effect of gamma irradiation (0 to 5 MRad) on the friction and wear properties of UHMWPE under dry conditions has been reported (ref. 3). In that study, sterilization doses of 2.5 and 5.0 megarads greatly altered the average molecular weight and molecular weight distribution of UHMWPE, but friction and wear properties of the polymer were not significantly changed. Shen and Dumbleton (ref. 4) have reported on the friction and wear behavior of polyethylene irradiated at higher levels (20 to 1000 MRad). In general, both friction and wear increased with increasing dose. Infrared analysis of their specimens indicated the presence of trans-unsaturation by the appearance of an absorption peak at a wave number of 966 cm^{-1} . Infrared analysis has also been used to detect polymer surface oxidation. Atkinson, et al. (ref. 5) reported the presence of carbonyl bonds in streamer wear debris from pin-on-disk tests. Distinct infrared absorption peaks were observed at 1724 cm^{-1} in thin sheets of hot pressed wear debris but not present in slivers of bulk UHMWPE hot pressed in the same way.

The presence of either unsaturation or carbonyl bonds would indicate that the polymer has been chemically degraded. This type of degradation may alter the boundary lubricating characteristics of the polymer (ref. 6 and 7).

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Internal reflection spectroscopy (ref. 8) is the technique of recording optical spectra by placing a material in contact with a transparent medium of greater refractive index and measuring the reflectance from the interface. If the material in contact with the transparent medium is absorbing, the reflectance for total internal reflection will be attenuated to some value between zero and unity in regions of the spectrum where absorption of radiant energy can take place. Therefore, the emerging beam will resemble the spectrum of the absorbing material as if it were measured by ordinary transmission techniques. The technique for obtaining spectra in this manner is called attenuated total reflection spectroscopy (ATR). Because the beam penetrates the absorbing material for a distance on the order of a wavelength of infrared light, ATR provides essentially a surface absorption spectrum.

The objective of this investigation was to analyze the surfaces and the bulk of ultrahigh molecular weight polyethylene wear test specimens using attenuated total reflection infrared spectroscopy.

TEST SPECIMENS

The test specimens were 0.476-centimeter radius hemispherically tipped riders approximately 2 centimeters in length. They were made of ultrahigh molecular weight polyethylene (RCH1000). The specimens were from a previous wear test program (ref. 3) and the details of their history appear in table I.

APPARATUS

An infrared grating spectrophotometer (Perkin-Elmer Model 221) was used for all measurements. An internal reflection attachment (fig. 1) (Harrick Instruments Corp.) was used in the sample space of the spectrophotometer. The radiation from the source is reflected by mirror M1 to enter the internal reflection plate (a 5 by 12 by 2 mm plate of pure germanium) and is returned in such a way that mirrors M2 and M3 bring it onto the spectrometer entrance slit with the same convergence it would have had in the absence of the attachment.

The angles of internal reflection within the plate are all greater than the critical angle (germanium-polyethylene), and the arrangement of the unit is such that five reflection will occur on either surface on the way into the reflection plate and five more on the way out, for a total of ten reflections. However, because of size limitations of the rider wear specimens, only a single reflection could be used for the wear surface and three for the reference or bulk material.

PROCEDURE

One 100 μm thick slice was cut from the end of the rider containing the wear scar. Three 100 μm slices were cut from the opposite end (discarding the extreme end, except for one sample). A precision biological microtome was used for the cutting operation. The slices were cleaned with water and detergent, rinsed with distilled water, then with alcohol, and finally with pentane and then dried.

The slices were placed on a well-cleaned germanium plate with the outer surfaces facing the plate (where applicable). Three full-diameter slices were placed on one side of the plate together, like pancakes on a griddle. However, slices containing the wear scars were placed alone on the plate. For this reason, the absorption bands of the references were always stronger than those of the wear scar surfaces.

The entire spectrometer was covered by a plastic enclosure and the assembly continuously flushed with air dried and cleaned of carbon dioxide by passing through a large column of Linde Molecular Sieve No. 5A.

RESULTS

The infrared spectrum for the unworn end of the 5 MRad irradiated specimen appears in figure 2(a). The surface facing the germanium plate was the flat, unworn end of the rider specimen. The procedure for removal of moisture and carbon dioxide was effective as evidenced by the lack of fine structure in the 1400 to 1800 cm^{-1} region. The most intense bands are at 2851 and 2919 cm^{-1} (C-H stretching), 1460 cm^{-1} (C-H deformation), and at 827 and 741 cm^{-1} (CH_2 rocking). These are bands that would be expected for a polyethylene surface (ref. 9).

There is a slight indication of a band at 1743 cm^{-1} , which would indicate the presence of carbonyl, but it is very weak. The spectrum of the wear scar surface for the 5 MRad specimen is shown in figure 2(b). This spectrum is identical to the one for the unworn surface (fig. 2(a)) with two exceptions. There is no indication of a band at 1743 cm^{-1} and a weak broad band is present from 3100 to 3300 cm^{-1} . This weak band probably is due to a small amount of moisture adsorbed on the surface.

The infrared spectra of the wear scar surface and the polymer interior for the 2.5 MRad specimen appear in figures 3(a) and (b), respectively. Again, these spectra appear identical. Both have the broad weak band centered at 3100 cm^{-1} and the other bands associated with polyethylene.

Figure 4 contains the corresponding spectra for the unirradiated polymer. The spectrum for the wear scar surface appears in figure 4(a) and the spectrum

for the polymer interior in figure 4(b). Both spectra are essentially the same and very similar to the spectra for the two irradiated specimens.

DISCUSSION

As briefly described in the introduction, the ATR spectrum is of the nature of a surface absorption spectrum. The intensity of the bands is a function of the "effective optical path" and is strongly dependent on the angle of incidence on the plate and sample. Multiple reflections build up the band intensities. However, as previously mentioned, only one reflection could be used for the wear surface and three for the bulk polymer because of size limitations. Accordingly, the intensities of the spectral bands are necessarily weak.

Taking this into account, there does not appear to be any significant polymer surface degradation (oxidation or unsaturation) resulting from either the irradiation procedure or the friction and wear process. It would follow that the surface adsorption characteristics of the irradiated polyethylene should not be grossly different from those for the virgin polymer.

Since the boundary lubricating characteristics are highly dependent on the adsorption of polar molecules onto the polymer surface, one would not expect gross differences in these characteristics either. Obviously, other factors, such as changes in polymer physical properties, may affect the boundary characteristics. However, the physical changes induced by the gamma irradiation did not alter the unlubricated friction and wear properties (ref. 3).

SUMMARY OF RESULTS

Attenuated total reflection infrared spectroscopy was used to analyze ultrahigh molecular weight polyethylene wear test specimens. The following results were obtained:

1. Neither gamma sterilization irradiation (to 5.0 MRad) nor the friction and wear process itself produced any substantial amount of polymer surface degradation.
2. The only spectral band detected on most of the polymer surfaces and not related to the polyethylene itself was a broad weak band centered at 3100 cm^{-1} . This was probably the result of a small amount of adsorbed moisture.
3. Therefore, it was concluded that the sterilization process should not alter the boundary lubricating properties of the polyethylene with regard to adsorption of lubricant surface active species.

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TABLE I. - HISTORY OF WEAR TEST SPECIMENS (REF. 3)

Specimen*	Load, N	Sliding speed, m/s	Sliding dist, m	Wear scar diameter, mm	Average friction coeffi- cient	Average wear rate, $\text{m}^3/\text{N}\cdot\text{m}$
Unirradiated	9.8	0.076	182 000	3.38	0.40	0.75×10^{-15}
2.5 MRad	9.8	.063	185 000	3.38	.45	$.76 \times 10^{-15}$
5.0 MRad	9.8	.076	93 500	2.86	.42	$.78 \times 10^{-15}$

*All specimens were run unlubricated in dry air against 316 L stainless steel disks.

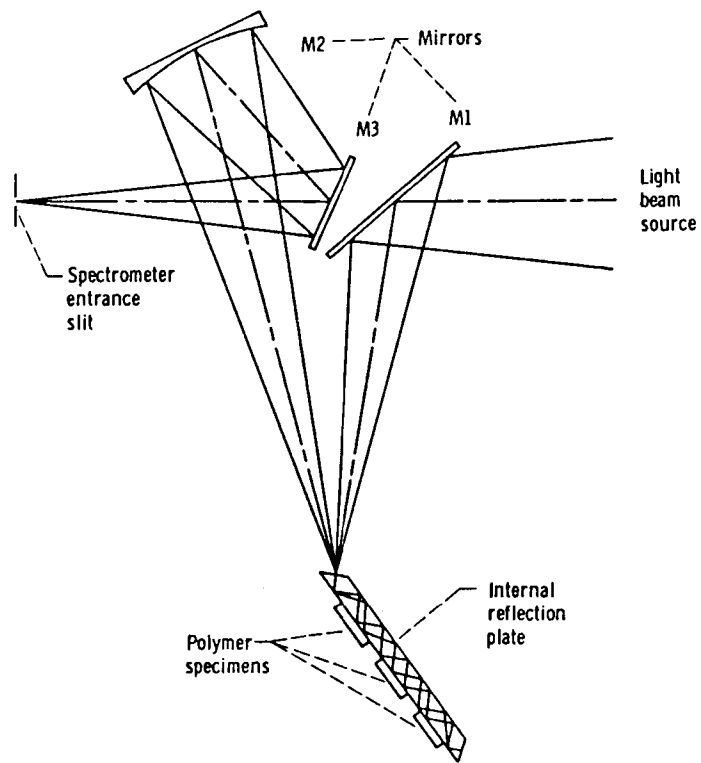


Figure 1. - Optical diagram of internal reflection attachment to infrared spectrometer.

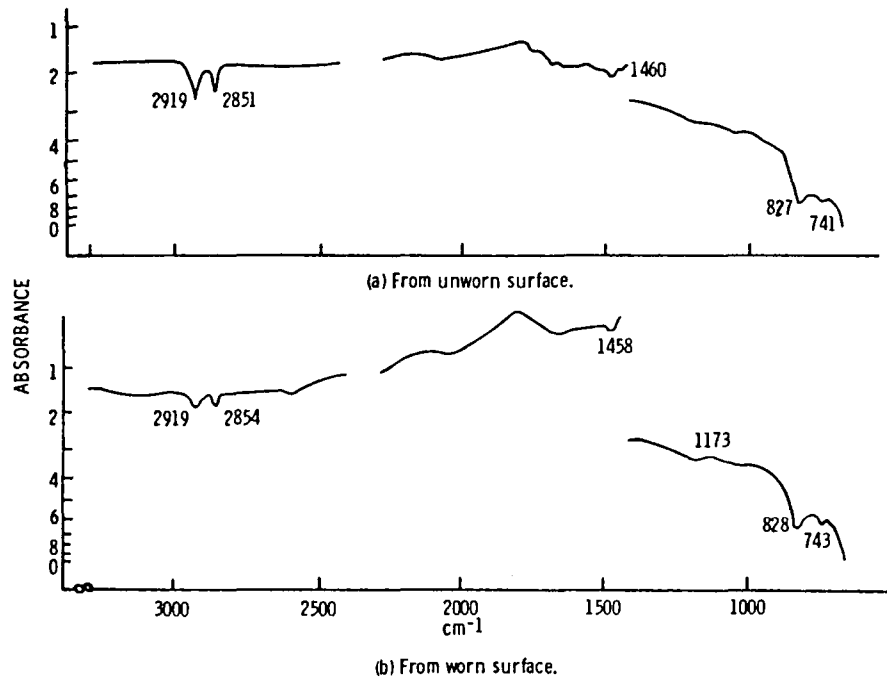


Figure 2. - Infrared absorption spectra from gamma irradiated polyethylene wear test specimen (5.0 mrad).

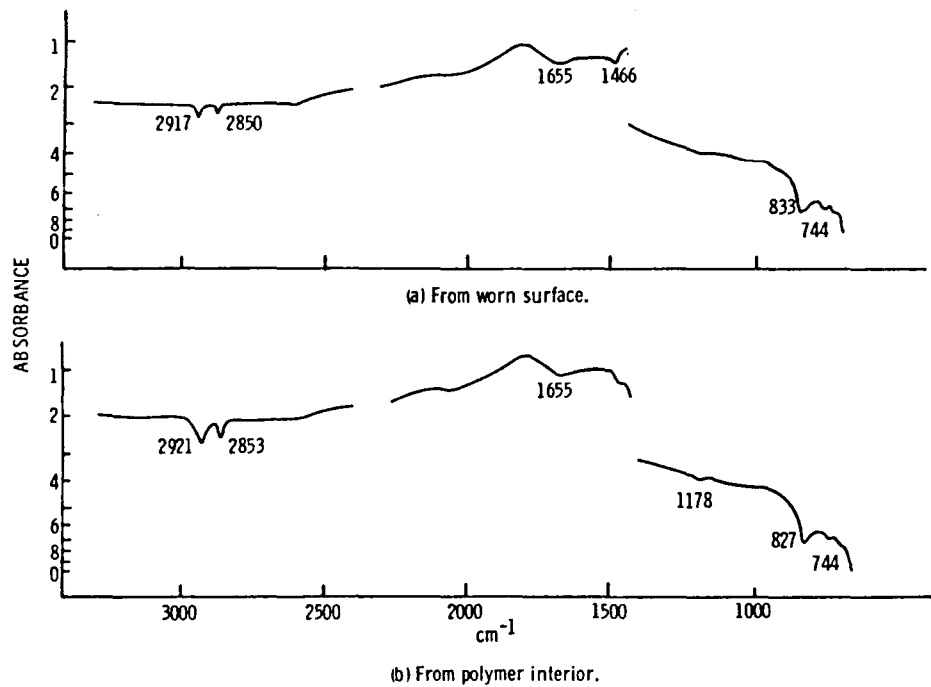


Figure 3. - Infrared adsorption spectra from gamma irradiated polyethylene wear test specimen (2.5 mrad).

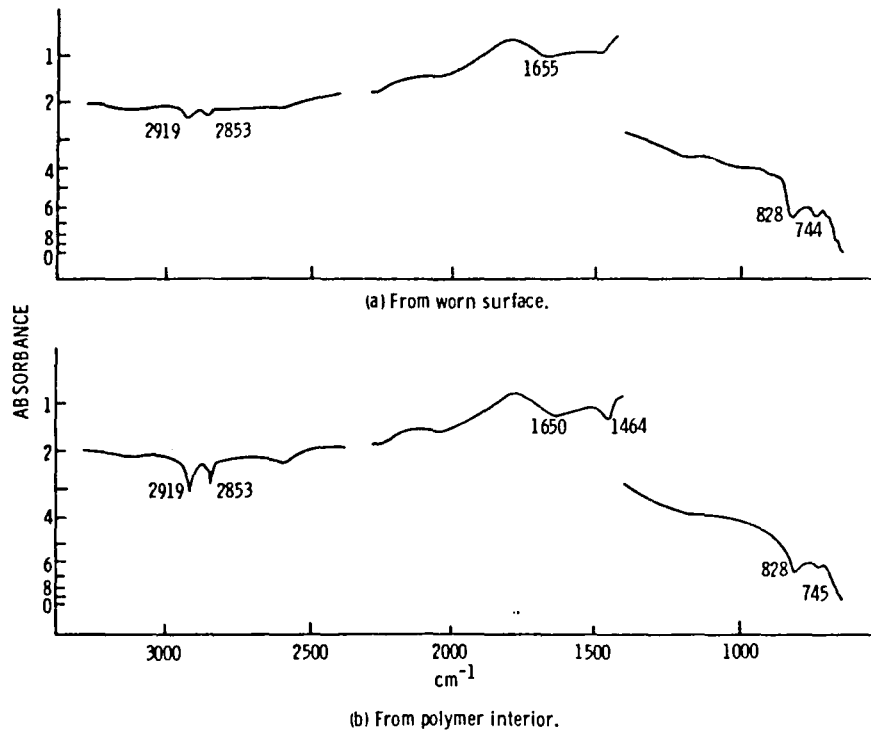


Figure 4. - Infrared absorption spectra from unirradiated polyethylene wear test specimen.

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