

Analysis of the Types and Amounts of Carbonyl Species Present in Oxidized Polyethylene

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Synopsis

The carbonyl species present in oxidized polyethylene are qualitatively and quantitatively determined through the use of infrared measurements on the polymer. The method described makes use of a carbon monoxide/ethylene copolymer wedge in the reference beam of the infrared spectrophotometer to compensate the large 1720 cm^{-1} ketone absorbance. This allows one to observe the 1710 cm^{-1} and 1735 cm^{-1} carbonyl absorbances as distinct peaks rather than as shoulders on the 1720 cm^{-1} peak. This is a significant advantage over other published infrared methods for this analysis. The absorbances obtained at 1710 cm^{-1} and 1735 cm^{-1} are then used in an equation to calculate the absorbance at 1720 cm^{-1} due to ketonic carbonyl only. Our results confirm Cooper and Prober's assignment of both the 1710 cm^{-1} and 1735 cm^{-1} absorbances in the infrared spectra of oxidized polyethylene to acid functionality. Our quantitative results are comparable to those reported by Cooper and Prober, and our method represents a significant reduction in the time required for the analysis (1.5 hr vs. ~ 45 days). The carbonyl distribution in a commercially oxidized polyethylene wax was determined as being ~ 11.0 ketone $\text{C}=\text{O}/2000\text{ C}$ and ~ 21.7 acid $\text{C}=\text{O}/2000\text{ C}$ (with a σ of $1.8\text{ C}=\text{O}/2000\text{ C}$ and $3.0\text{ C}=\text{O}/2000$, respectively). A high-density polyethylene, oxidized with air in the laboratory, contained ~ 1.91 ketone $\text{C}=\text{O}/2000\text{ C}$ and 2.19 acid $\text{C}=\text{O}/2000\text{ C}$ (with a σ of $0.08\text{ C}=\text{O}/2000\text{ C}$ and $0.16\text{ C}=\text{O}/2000\text{ C}$, respectively).

INTRODUCTION

The properties of polyethylene are affected by the amount and type of carbonyl species present in the polymer. For example, it has been shown that polymer oxidation plays an important role in the adhesion of polyethylene to metals.^{1,2} Also, the emulsifiability of oxidized polyethylene depends on the acid content of the polymer as described in numerous U.S. patents.^{3,4} Therefore, a method for determining the type and amount of carbonyl species present in oxidized polyethylene is very important commercially as well as in the elucidation of the mechanisms involved in these processes.

The early literature pertaining to this subject consists mainly of qualitative infrared studies. Between 1945 and 1950, most authors agreed that the carbonyl absorbance in the infrared spectrum of oxidized polyethylene is largely due to ketonic carbonyl groups.^{5,6,7} Some stated that it is all due to ketonic groups.⁵ Others felt that there is also some acid present.⁶ Still others stated that the absorbance is due entirely to aldehydic or ketonic carbonyl groups.⁷ The inability of the instruments used in these studies to resolve the various carbonyl groups is apparently the main reason for this difference of opinion.⁸

In 1959, Rugg, Smith, and Bacon⁸ using a double-beam grating spectrophoto-

tometer concluded that the majority of the carbonyls present in highly heat-oxidized film were ketonic, with small contributions from acid and aldehyde. However, their data showed that photo-oxidized film had about equivalent aldehyde, ketone, and acid absorbances. They estimated the carbonyl content of these highly oxidized films at ~ 5 carbonyl groups per 2000 carbon atoms ($C=O/2000 C$).

Lanceley⁹ reports that he obtained about the same results as Rugg, Smith, and Bacon. The largest absorptions at 1709 cm^{-1} and 1723 cm^{-1} were identified respectively as carboxylic acid and ketonic carbonyls. He states that distinct shoulders provide evidence for aldehyde groups and possibly ester groups, but these are present in much lower concentrations.

Wood and Luongo¹⁰ reported that, based on the wavelength of the absorbances, the carbonyl species present in thermally oxidized polyethylene (DYNK) are mainly ketonic, with lesser amounts of ester, acid, and aldehyde.

In 1960, Cooper and Prober¹¹ of General Electric described their studies on the action of oxygen corona and ozone on polyethylene. Their characterization of the carbonyl types present in film oxidized with ozone and the corona discharge indicated that the main absorbance was consistent with ketone or associated carboxylic acid groups. They further state that, although the shoulder observed at 1735 cm^{-1} is consistent with aldehyde groups, they believe it is due principally to unassociated carboxylic acid groups. The experimental approach used by Cooper and Prober was to convert the carboxylic acid to a salt by placing the oxidized film in $0.2N$ NaOH and to periodically measure the change in the carbonyl absorbance at 1720 cm^{-1} . When this absorbance stopped decreasing, they assumed that all of the acid had been converted to salt (this took ~ 45 days). Their evidence for assigning the shoulder at 1735 cm^{-1} to acid is that it disappeared after neutralization and reappeared after the neutralized film was soaked in $0.2N$ H_2SO_4 in 95% EtOH. Based on the size of the remaining peak versus the size of the peak before neutralization, they concluded that 38–49% of the carbonyl absorbance present in these films was due to ketone and the rest, due to acid absorbance.

In our study of oxidized polyethylene, we were interested in developing a practical method for the quantitative determination of carbonyl species. The approach we chose for this analysis is somewhat novel in that we canceled the 1720 cm^{-1} (ketone) absorbance with a wedge of carbon monoxide/ethylene copolymer in the reference beam of the infrared spectrophotometer. This resulted in the ability to observe the absorbances at 1710 cm^{-1} and 1735 cm^{-1} as peaks rather than as shoulders on the main 1720 cm^{-1} peak.

Using this in combination with neutralization techniques on commercially oxidized waxes, we established a totally infrared method for quantitatively determining the carbonyl species present in oxidized polyethylene.

EXPERIMENTAL

In order to establish a method that uses only infrared measurements, we had to determine how much the neighboring absorbances at 1710 cm^{-1} and 1735 cm^{-1} contribute to the main absorbance at 1720 cm^{-1} . Once this was done, the absorbance at 1720 cm^{-1} due to ketonic carbonyl only could be determined. We accomplished this by measuring the absorbances per unit path length (A') at 1710

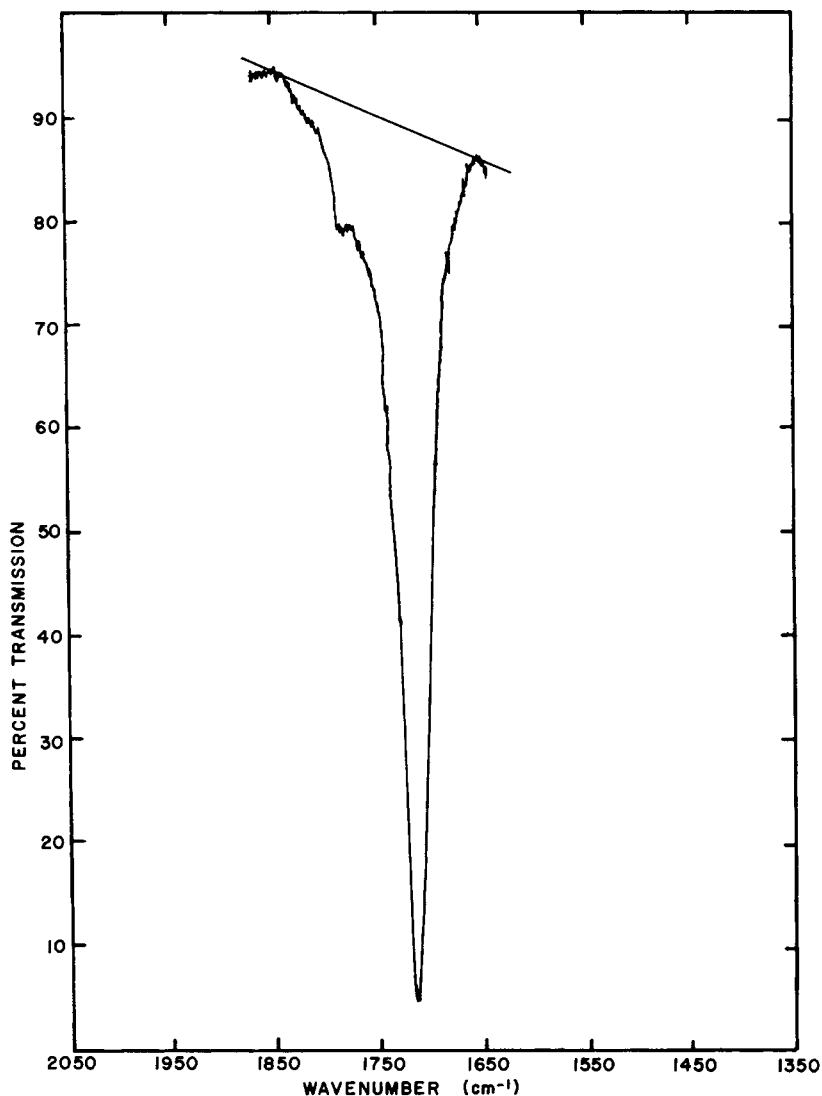


Fig. 1. Infrared spectrum of oxidized polyethylene between 1650 cm^{-1} and 1850 cm^{-1} .

cm^{-1} , 1720 cm^{-1} , and 1735 cm^{-1} as described below, in three commercially oxidized polyethylene waxes, titrating the acid present, and remeasuring the infrared absorbances.

Infrared Analysis. The oxidized polyethylene was pressed between Mylar sheets into a thin film (~ 0.03 – 0.07 mm) using a Pasadena Hydraulics press with heated platens. The IR spectrum was scanned between 1650 cm^{-1} and 1850 cm^{-1} using a Beckman IR-12 double-beam infrared spectrophotometer with filter/grating optics. The baseline was drawn and the A' at 1720 cm^{-1} measured (see Fig. 1). Next, a wedge of a carbon monoxide/ethylene copolymer was placed in the reference beam of the spectrophotometer and the pen brought back to the baseline at 1720 cm^{-1} by adjusting the wedge so that the energy absorbed in the reference beam equaled that absorbed in the sample. When this was accomplished, the compensated spectrum was scanned between 1650 cm^{-1} and 1850

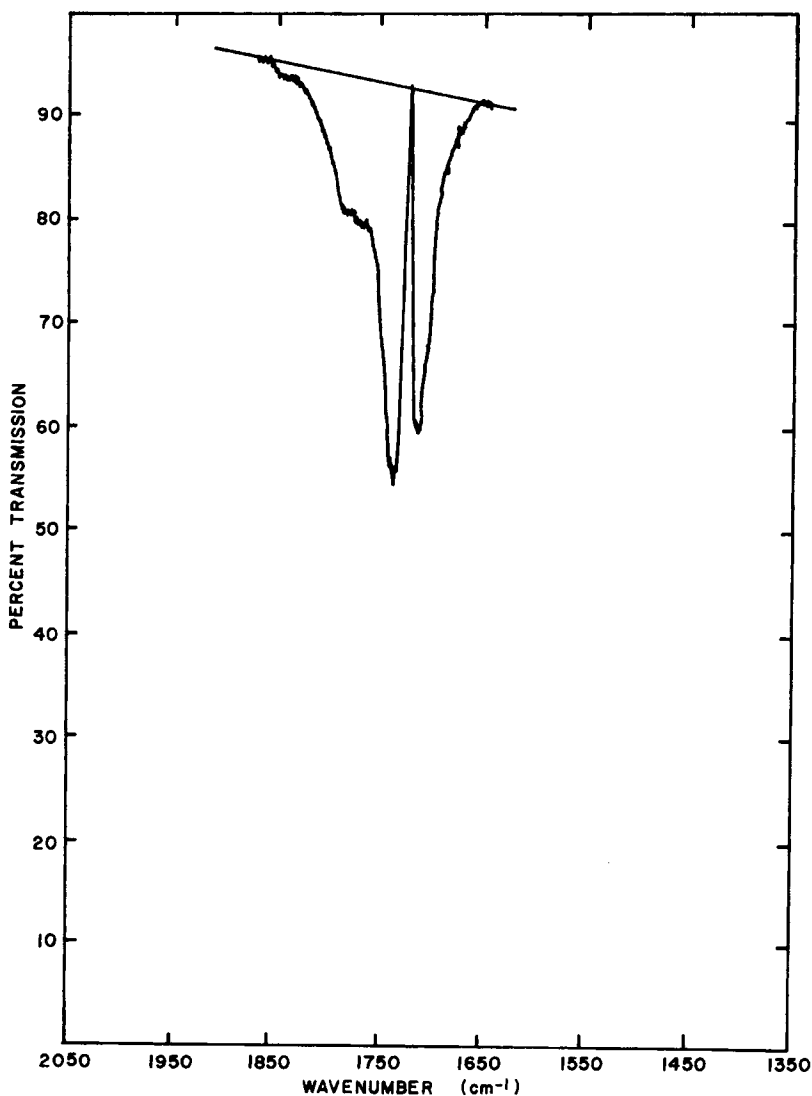


Fig. 2. Infrared spectrum of oxidized polyethylene between 1650 cm^{-1} and 1850 cm^{-1} following compensation of the ketone carbonyl absorbance at 1720 cm^{-1} .

cm^{-1} , the baseline drawn, and the resulting A' at 1710 cm^{-1} and 1735 cm^{-1} measured (see Fig. 2).

Acid Titration. Two grams of the oxidized polyethylene wax was dissolved by refluxing in 135 ml xylene and 35 ml pyridine in a round-bottom flask equipped with a condenser, heating mantle, and magnetic stirrer. The solution was removed to a fume hood, allowed to cool for about 5 min, then stirred and titrated to a phenolphthalein endpoint with $0.025N$ sodium hydroxide in methanol.

Recovery of the Sample for Infrared Analysis. After the acid had been titrated, the sample was precipitated by pouring into cold methanol. The precipitate was filtered, washed with methanol, and dried in a vacuum oven at 75°C for 1 hr. Following this, the sample was analyzed by IR as described above.

RESULTS AND DISCUSSION

Our IR data after neutralization indicated that the 1735 cm^{-1} absorbance had been reduced by the neutralization. This supports Cooper and Prober's assignment of this absorbance to acid functionality.

However, the neutralization apparently had not converted all of the acid present to the salt since an absorbance still remained at 1710 cm^{-1} as well as at 1735 cm^{-1} . The per cent neutralization, as calculated based on the disappearance of the absorbances at 1735 cm^{-1} and 1710 cm^{-1} , indicated that only $\sim 65\%$ of the acid present had been neutralized by the titration. Even after refluxing the sample with excess NaOH, IR indicated only $\sim 75\%$ neutralization.

We also found that when we neutralized these waxes as a melt with zinc acetate in a Thropp mill, only $\sim 80\%$ neutralization was achieved. It appears that it may be rather difficult by these techniques to completely neutralize these waxes.

At any rate, this caused a slight problem for us in that by neutralization we could not completely remove the acid contributions from the total carbonyl to calculate the ketone content. This was overcome, however, by using the following approach.

Since the total carbonyl absorbance at 1720 cm^{-1} is due to the ketone absorbance, plus some contribution from the 1735 cm^{-1} and some contribution from the 1710 cm^{-1} absorbances, the following equation may be written:

$$Y_{\text{total}} = y + ax + bz \quad (1)$$

where Y_{total} = the total, uncompensated absorbance per unit thickness (A') at 1720 cm^{-1} ; y = the contribution to the absorbance due to ketone; x = the A' at 1735 cm^{-1} in the compensated spectrum; z = the A' at 1710 cm^{-1} in the compensated spectrum; and a , b = proportionality constants.

Since we had data on the total absorbance at 1720 cm^{-1} using the spectra as is, and the 1735 cm^{-1} and 1710 cm^{-1} absorbances from the compensated spectra, the unknowns in the equation are y , a , and b .

Furthermore, these data were available for the waxes, as is, after neutralization and after further neutralization (refluxed with NaOH). Therefore, the following set of three equations in three unknowns was written:

$$\begin{aligned} Y_{\text{total}_1} &= y + ax_1 + bz_1 \\ Y_{\text{total}_2} &= y + ax_2 + bz_2 \\ Y_{\text{total}_3} &= y + ax_3 + bz_3 \end{aligned} \quad (2)$$

where $Y_{\text{total}_{1,2,3}}$ = the uncompensated total A' at 1720 cm^{-1} for the wax as is, after neutralization, and after further neutralization; y = the A' due to ketone $\text{C}=\text{O}$; $x_{1,2,3}$ = the A' at 1735 cm^{-1} in the compensated spectrum of the wax as is, after neutralization, and after further neutralization; $z_{1,2,3}$ = the A' at 1710 cm^{-1} in the compensated spectrum of the wax as is, after neutralization, and after further neutralization; and a , b = proportionality constants.

The data for the three waxes were treated in this way, and fairly good agreement resulted for the constants a and b . The final equation using the average values of a and b and after rearrangement is as follows:

$$y = Y_{\text{total}} - 1.37x - 0.18z \quad (3)$$

where y = the A' at 1720 cm^{-1} due to ketone $\text{C}=\text{O}$ only; Y_{total} = the A' at 1720

cm^{-1} in the uncompensated spectrum of the polymer as is; $1.37 =$ the proportionality constant a ; $x =$ the A' at 1735 cm^{-1} in the compensated spectrum of the polymer as is; $0.18 =$ the proportionality constant b ; and $z =$ the A' at 1710 cm^{-1} in the compensated spectrum of the polymer as is.

Therefore, the A' at 1720 cm^{-1} due to ketonic carbonyl species absorbing in the IR spectrum of oxidized polyethylene can be calculated using eq. (3) and the values of Y_{total} , x , and z .

Six films of one of the commercial waxes were pressed and analyzed using the compensation/IR technique to obtain the Y_{total} , x , and z values. The A' at 1720 cm^{-1} due to ketonic carbonyl only was then calculated from these values and eq. (3). The results are summarized in Table I. They indicate that $\sim 39\text{--}47\%$ of the total carbonyl absorbance observed is due to ketone. This agrees well with the $38\text{--}49\%$ of the absorbance reported by Cooper and Prober as being due to ketone in their studies on oxidized polyethylenes.

Once the A' due to ketonic carbonyl had been determined, the ketone concentration in the sample was calculated using an absorptivity obtained by measuring the A' of a standard carbon monoxide/ethylene copolymer. The ketone content of this copolymer was established by neutron activation analysis for oxygen.

In addition, a calibration curve was needed to determine the acid content of the oxidized polyethylenes. Since our data indicate that the acid titration does not reflect the total acid content of these waxes, and since both the 1735 cm^{-1} and 1710 cm^{-1} absorbances appear to be due to acid (according to Cooper and Prober's data as well as our own), the decrease observed for these two absorbances after neutralization was added together and plotted against the titrated acid content. This calibration curve is shown in Figure 3.

Therefore, the total acid content of the oxidized waxes is calculated using this calibration curve and the sum of the 1735 cm^{-1} and 1710 cm^{-1} A' in the compensated spectra of the waxes.

A measure of the precision of this analysis was obtained by determining the ketone and acid contents for the six pressed films from the commercial wax. These results are summarized in Table II. The wide variation observed in these results is mainly due to heterogeneity in the oxidized material. This is not surprising in a process involving a gas-melt interaction as in the case of the oxidation of polyethylene.

TABLE I
Calculated A' Due to Ketone Carbonyl Only at 1720 cm^{-1}
in a Commercially Oxidized Wax

Film no.	Total A' at 1720 cm^{-1} in the film as is	Calculated A' due to ketone C=O	Total absorbance due to ketone, %
1	34.9	14.8	42.4
2	24.4	10.6	43.4
3	26.0	10.1	38.9
4	27.2	12.7	46.7
5	32.1	14.3	44.5
6	32.2	15.2	47.2
			Avg. = 43.8%

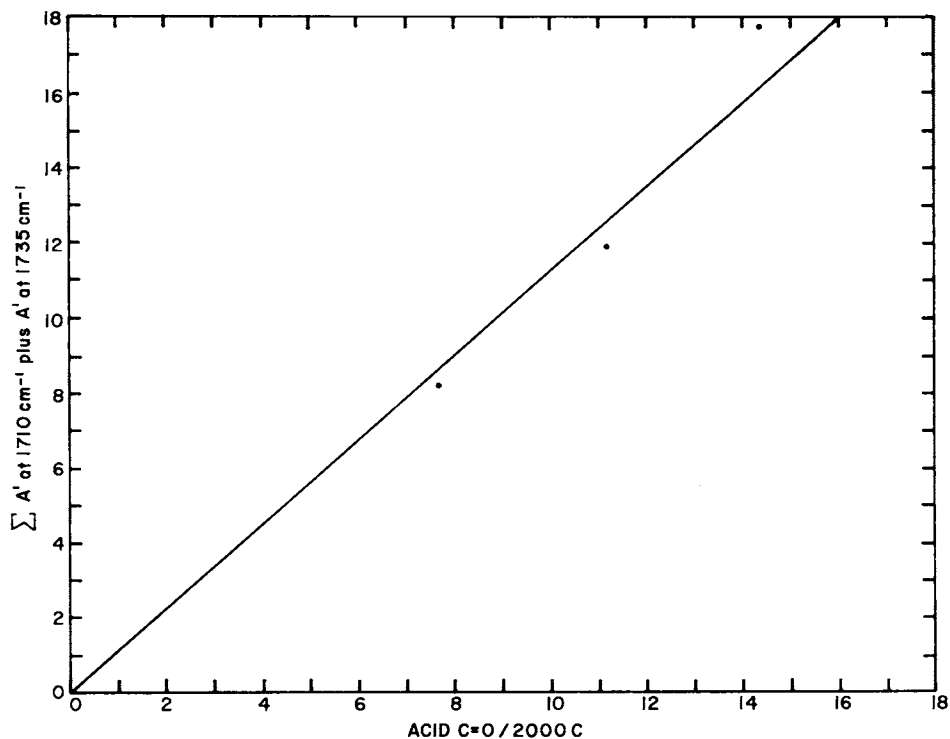


Fig. 3. A' for the 1710 cm^{-1} absorbance plus A' for the 1735 cm^{-1} absorbance vs. acid $\text{C}=\text{O}/2000\text{ C}$.

To further confirm that the only carbonyl species present in these samples are ketonic and acidic, the following experiment was done. Films of the oxidized wax were immersed in $1.0N$ NaOH in 95% ethanol at 50°C for two weeks. Infrared analyses were then carried out on these samples following this extended NaOH treatment. When the ketone carbonyl in these films was compensated with the $\text{CO}/\text{C}_2\text{H}_4$ wedge in the reference beam, no absorbances in the carbonyl region remained. This confirms that only acid and ketone carbonyl species are present in these samples.

In addition, six films of a high-density polyethylene sample, oxidized to a lower level in the laboratory, were analyzed using the compensation/IR method. This

TABLE II
The Ketone and Acid Carbonyl Contents of a Commercially Oxidized Wax

Film no.	Ketone $\text{C}=\text{O}/2000\text{ C}$	Acid $\text{C}=\text{O}/2000\text{ C}$
1	12.6	26.7
2	9.0	18.6
3	8.6	20.3
4	10.8	19.2
5	12.1	23.1
6	12.9	22.1
	Avg. 11.0	21.7
	σ 1.8	3.0

TABLE III
The Ketone and Acid Carbonyl Contents of a High-Density Polyethylene
Oxidized with Air in the Laboratory

Film	Ketone C=O/2000 C	Acid C=O/2000 C
1	1.94	2.14
2	1.87	1.98
3	2.04	2.15
4	1.94	2.14
5	1.82	2.45
6	1.86	2.29
	Avg. 1.91	2.19
	σ 0.08	0.16

sample had been oxidized as a melt with good mixing in the presence of air. The data for this study are summarized in Table III. Although these levels are about ten times lower than those of the commercial wax, the precision is better. Therefore, this sample oxidized to a lower level appears to be more homogeneous and the method seems to have sufficient precision.

CONCLUSIONS

Through the use of our infrared compensation technique and eq. (3), we arrived at the same results as Cooper and Prober for how much of the total absorbance at 1720 cm^{-1} in oxidized polyethylene is due to ketonic carbonyls. Since we mathematically eliminated the 1710 cm^{-1} and 1735 cm^{-1} absorbances and they arrived at their result by converting all the acid present to salt, our work confirms the assignment of the 1735 cm^{-1} as well as the 1710 cm^{-1} absorbances to acid functionality. In addition, an extended neutralization with NaOH eliminated the 1710 cm^{-1} and 1735 cm^{-1} absorbances in the compensated spectra of the oxidized polyethylene waxes. We, therefore, feel that the carbonyl species present in oxidized polyethylene are predominantly ketonic and acidic.

In addition, our method represents a substantial reduction in the time required for this analysis. Once the equation has been set up (this need be done only once), the analysis requires only ~ 1.5 hr per sample.

A significant advantage of our infrared compensation technique over other published infrared studies of oxidized polyethylene is the ability to "observe" the shoulders at 1710 cm^{-1} and 1735 cm^{-1} as peaks by eliminating the 1720 cm^{-1} ketone absorbance through the use of the carbon monoxide/ethylene copolymer wedge in the reference beam of the infrared spectrophotometer.

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