

IR Spectroscopy Study of Polypropylene Natural Aging

A. RJEB,¹ L. TAJOUNTE,¹ M. CHAFIK EL IDRISSE,¹ S. LETARTE,² A. ADNOT,² D. ROY,² Y. CLAIRE,³
A. PÉRICHAUD,³ J. KALOUSTIAN⁴

¹ Laboratoire de Physique de Surfaces et Interfaces, Département de Physique, Université IBN TOFAIL BP 133, Kénitra, Maroc

² Laboratoire de Physique Atomique et Moléculaire, Centre de Recherche sur les Propriétés des Interfaces et la Catalyse, Pavillon Vachon, Université Laval, Cité Universitaire, Québec, G1K 7P4 Canada

³ Laboratoire de Chimie Macromoléculaire, Université de Provence, 3 Place Victor Hugo, F-13331 Marseille, Cedex 3, France

⁴ Laboratoire de Chimie Analytique, 27 Bd. J. Moulin, F-13385 Marseille, Cedex 5, France

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ABSTRACT: Structural modifications of a commercial polypropylene (PP) sample are studied by IR spectroscopy. Aging this sample under an ambient atmosphere with or without the presence of ambient light shows the oxidation process to be the most predominant. Spectral analysis reveals that the commercial sample is isotactic and also indicates that, for the new sample, oxygen establishes single bonds with carbon. However, through the aging process, spectral changes essentially occur in the regions of ~ 3400 , ~ 1712 , and 1170 cm^{-1} which correspond to hydroxyl and/or hydroperoxide groups, a carbonyl group, and C—O, respectively. The deconvolution of the bands corresponding to a carbonyl group reveals the presence of a complicated mixture of oxidation products: aldehydes, ketones, esters, acids, peresters, and peracids. Spectral analysis also shows that the most favorable site for oxidation is at the methylene group.
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Key words: polymer; polypropylene; aging; oxidation; FTIR

INTRODUCTION

The aging of a polymer is a slow and irreversible evolution of the properties of materials. Several analytical techniques can be used to determine these properties. Specifically, to study volume transformations, thermogravimetric analysis allows for the determination of weight loss upon heating while differential thermal analysis mea-

sures temperatures pertaining to physical transformations and enthalpy variations.¹ These studies showed that the degradation of the properties of a polymer begins on its surface. X-ray photoelectron spectroscopy (XPS) recently allowed us to probe the surface in order to determine the changes caused by various types of aging.² The results of this study showed that the important degradation to which the polymer surface is subjected came from polymeric oxidation. This degradation of the surface led us to use IR spectroscopy to further study these samples.

IR spectroscopy can be of the utmost importance in the analysis of industrial products for the

Correspondence to: D. Roy (droy@phy.ulaval.ca).
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detection of surface modifications caused by aging or a chemical reaction.

In this work IR spectroscopy was used for the structural analysis of three types of commercial polypropylene (PP) samples: completely new and unaged, aged under an ambient atmosphere but protected from ambient light, and aged under both, ambient atmosphere and ambient light.

EXPERIMENTAL

Polymer films were analyzed by absorption IR spectroscopy. The IR spectra (400 scans at 4 cm^{-1} resolution) were recorded at room temperature with a Mattson Series 100 Fourier transform spectrophotometer. The radiation was polarized with a rotating wire-grid polarizer (Specac) mounted in front of the sample; a reference spectrum was collected for each polarization. IR dichroic ratios were calculated from the peak height intensity measured in absorbance. All spectra manipulations were executed with SpectraCalc software (Galactic Industries Co.).

RESULTS

The IR spectrum of the new PP sample is shown in Figure 1. It consists of the characteristic bands of PP³: a broad and intense band that extends from 2860 to 3000 cm^{-1} is attributed to the valence vibrations of the C—H bonds, a band located at 1460 cm^{-1} is characteristic of methylene CH_2 groups, and a band at around 1378 cm^{-1} is attributed to the methylene CH_3 group. There are two other types of bands present: C—C vibrations are found in the lower frequency region (from 1000 to 840 cm^{-1}), and another band of intensity comparable to the former, which characterizes dialkyl ether bonds, C—O—C,⁴ is found at 1168 cm^{-1} . Note also the emergence of a very low intensity band at 1646 cm^{-1} that corresponds to C=C bonds,⁵ as well as the existence of another band, also of very weak intensity, in the region of $3114\text{--}3255\text{ cm}^{-1}$ that is attributed to the valence vibrations of an alkene C—H bond.

Figure 2 shows the spectrum of the sample aged under an ambient atmosphere but unexposed to ambient light. In addition to the characteristic bands next to the bands corresponding to the PP bonds (C—H, CH_2 , CH_3),³ the spectrum reveals the existence of a new band centered at

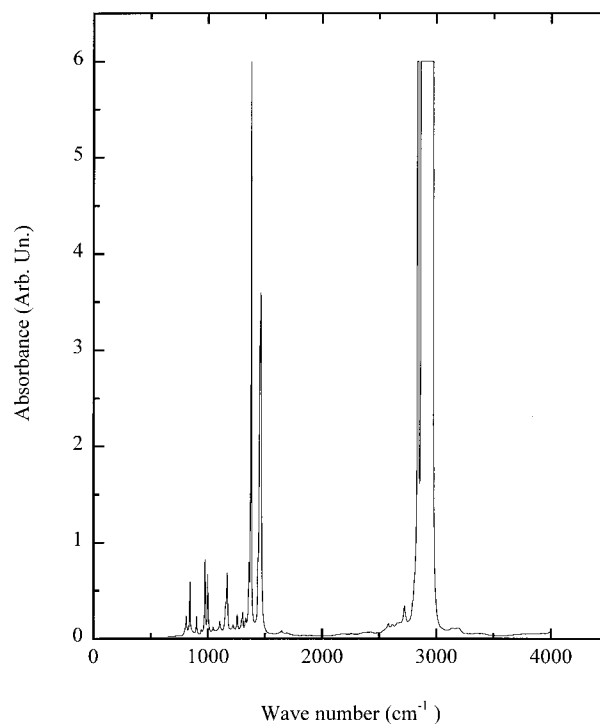


Figure 1 IR survey spectra of the new polypropylene sample.

1712 cm^{-1} that corresponds to a carbonyl bond C=O.³⁻⁶ Also, another new band between 3100 and 3500 cm^{-1} is attributed to a hydroxyl bond and/or hydroperoxide bond.⁴⁻⁶ Note the significantly increased intensity of the band located at 1168 cm^{-1} , which characterizes the C—O bond, and the decreased intensity of the band, corresponding to methylene $\text{—CH}_2\text{—}$ groups.

Figure 3 is the IR spectrum of the third PP sample, which was aged under both an ambient atmosphere and ambient light. It shows an important increase of the bands attributed to C=O, C—O, and OH bonds.

The changes that affect the three spectra of the corresponding PP samples essentially refer to these regions: ~ 3400 , 1712 , and $\sim 1170\text{ cm}^{-1}$. These regions respectively show the contributions from the alcohol and/or hydroperoxide groups, the carbonyl group (C=O), and C—O. The superposition of the region located between 1900 and 1550 cm^{-1} for the spectra of all three samples (Fig. 4) shows in particular that the carbonyl group is absent from the spectrum for the new PP sample while the second sample offers a very significant C=O feature, which is even more remarkable for the third sample (aged under an ambient atmosphere and ambient light).

For this current study the decomposition (or deconvolution) of the experimental spectra was achieved with the aid of SpectraCalc software. The operation consisted of representing the experimental spectrum by a theoretical function, which is the sum of several components with well-defined physical meanings.

Thus, for the new sample (Fig. 5) the deconvolution of the band located between 1900 and 1550 cm^{-1} shows the presence of three components centered at 1698, 1646, and 1638 cm^{-1} . This indicates the presence of a C=C bond in different environments. For instance, the band at ~ 1638 cm^{-1} corresponds to an unsaturated vinyl-type bond.^{5,7}

Moreover, for the sample aged under an ambient atmosphere but hidden from solar radiation, the deconvolution resulted in five components (Fig. 6). The first is located at 1637 cm^{-1} and may be attributed to single C=C bonds conjugated among themselves and/or with carbonyl groups. The second is located at 1700 cm^{-1} and is attributed to a conjugated ketone or to an amide functional group. The third component is centered at 1710 cm^{-1} and corresponds to a C=O that could

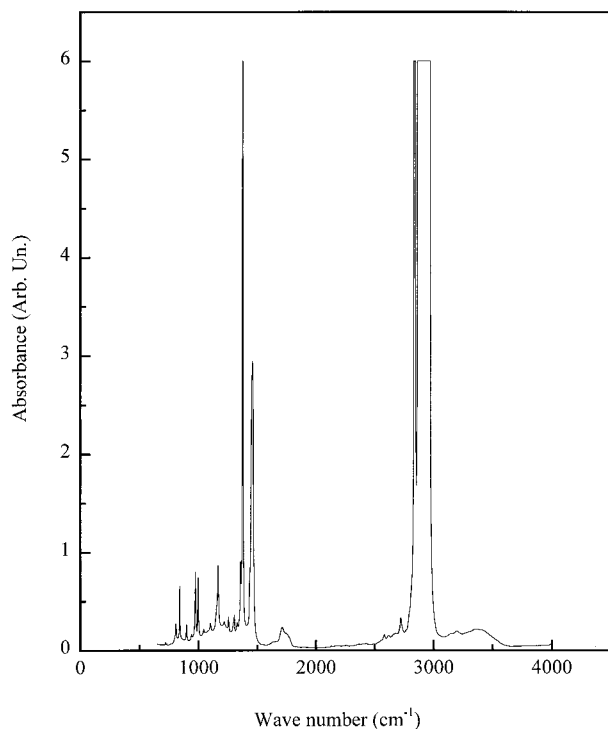


Figure 2 IR survey spectra of the polypropylene sample aged under an ambient atmosphere and protected from ambient light.

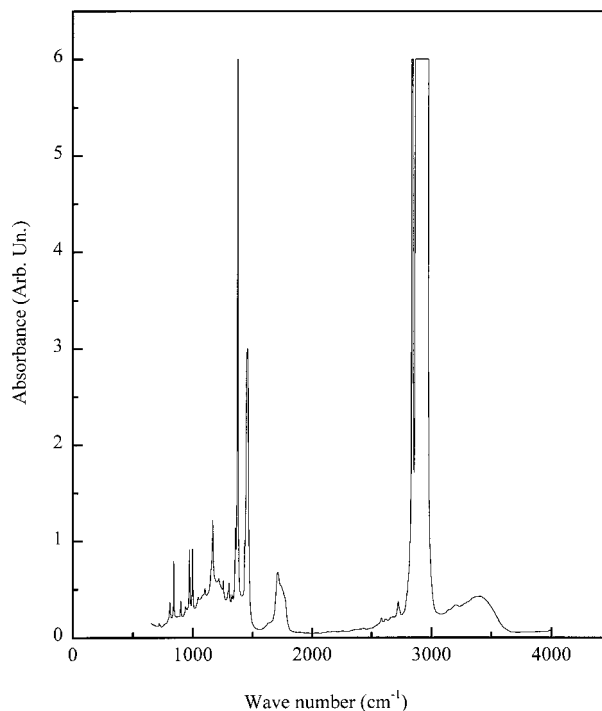


Figure 3 IR survey spectra of the polypropylene sample aged under an ambient atmosphere and ambient light.

originate from either a ketone, an aldehyde, or an acid.⁸ The fourth component found at 1751 cm^{-1} corresponds to a free acid and/or an ester. The fifth band, which is located at 1779 cm^{-1} , is attributed to a peracid group and/or a perester group or to a γ -perlactone.^{4-6,8}

However, the third sample, which was aged under an ambient atmosphere and solar radiation, showed the deconvolution of the experimental band (Fig. 7) to be formed of four components located at 1640, 1710, 1751, and 1777 cm^{-1} that correspond to C=C, an acid dimeric form and/or ketone or aldehyde, a free acid and/or ester, and a peracid and/or perester, respectively. Note the increased intensity of these different bands compared to those of the second sample, as well as the absence of the band centered at 1700 cm^{-1} that is attributed to a conjugated ketone or to an amide functional group.

DISCUSSION

In addition to the characteristic bands corresponding to the main groups found in the mate-

rial ($-\text{CH}$, $-\text{CH}_2$, $-\text{CH}_3$), the IR spectrum of the new PP sample also contains a band related to an ether's C—O bond. The existence of this band, which was confirmed by XPS,² indicates that oxygen is singly bonded in the polymer.

The method proposed by Luongo⁷ was used to determine the nature of the configurations of the chains forming the samples. This method is based on the characteristic absorption bands and those specific to the isotactic and atactic phases; its advantage is that it is independent of the physical nature of the samples and the molecular mass distribution and it is also unaffected by minor constituents such as stabilizers. For more information on the spectral differences characterizing the PP samples called 100% isotactic and 100% atactic, the reader may refer to Luongo.⁷ The IR spectrum of the new sample (Fig. 1) closely resembles that of the 100% isotactic; in particular, the two bands at 974 and 975 cm^{-1} have almost the same intensity (although these two bands show up in our instrument at 972 and 997 cm^{-1} , they are essentially the same) and the band at

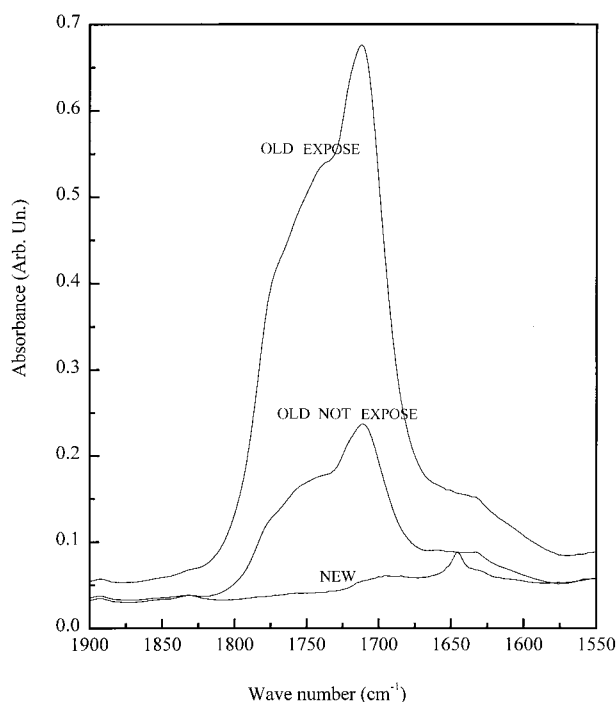


Figure 4 IR spectra from CO groups' characteristic region for (a) a nontreated polypropylene sample, (b) aged under an ambient atmosphere and protected from ambient light, and (c) aged under an ambient atmosphere and ambient light.

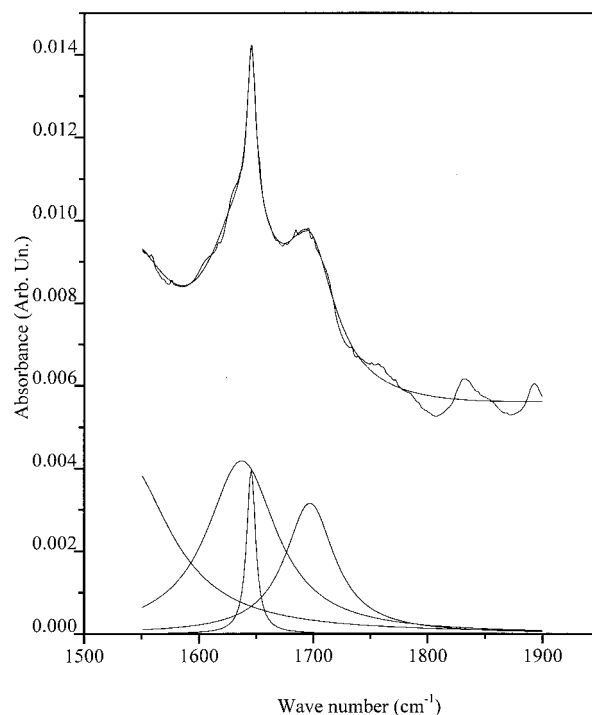


Figure 5 IR spectra of the new polypropylene sample that shows the deconvolution of the band located between 1900 and 1500 cm^{-1} , corresponding to the C=C bonding.

1168 cm^{-1} with a shoulder at 1554 cm^{-1} is also similar to the bands found on the 100% isotactic spectrum.

The fixation of oxygen on the polymer is caused by photooxidation reactions.⁹ PP is susceptible to oxidation by several methods: heating, γ radiation, UV, and so forth.¹⁰⁻¹⁴ Because the formation of the carbonyl group is always significant, certain authors follow the evolution of the carbonyl group as a function of exposure time.¹⁵⁻¹⁷ In this study the interest was on the nature of carbonyl-containing compounds. Hence, the different number of peaks arising from the deconvolution of this band for the second sample (five components) and the third sample (four components) is an interesting feature. It looks as though the disappearance of the component located at 1700 cm^{-1} is caused by one of the following three factors: First, it may be due to the cleavage of the conjugation between the ketone group and the C=C, especially because this latter band is observed at 1637 cm^{-1} for the sample aged under an ambient atmosphere but not exposed to solar radiation and is

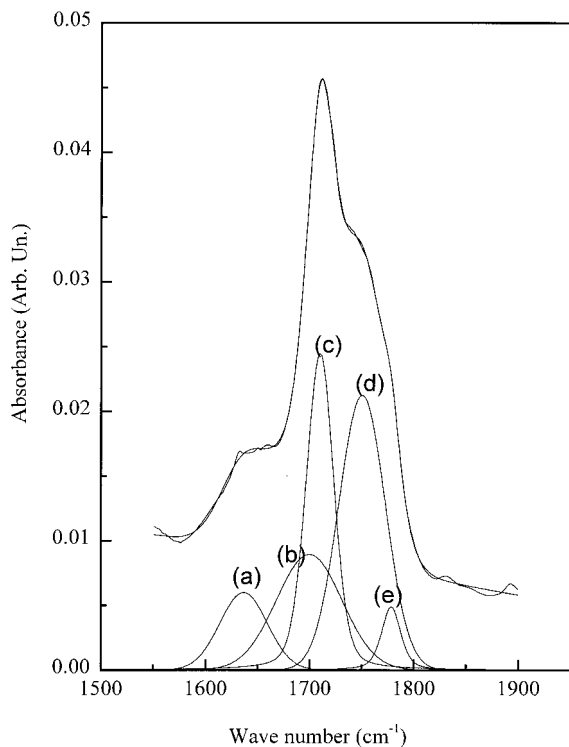


Figure 6 IR spectra of the polypropylene sample aged under an ambient atmosphere and protected from ambient light, which shows a five-peak deconvolution: (a) C=C conjugated among themselves and/or with carbonyl groups at 1637 cm^{-1} , (b) an amide functional group at 1700 cm^{-1} , (c) C=O at 1710 cm^{-1} , (d) free acid and/or ester at 1779 cm^{-1} , and (e) a peracid group and/or perester group at 1779 cm^{-1} .

seen at 1640 cm^{-1} on the spectrum of the sample aged under both an ambient atmosphere and ambient light. Second, the loss of the carboxylic acid existing as a dimer⁸ displaces ketones⁴ by $10\text{--}20\text{ cm}^{-1}$ and consequently would force the component appearing at 1700 cm^{-1} to add to the component found at 1710 cm^{-1} . Third, the last of these factors that could explain the disappearance of one of the five components is the possible photolysis of the amide functional group. Indeed, Dilks¹⁸ showed in a study of the natural aging of nylon-6,6 that the decrease of the nitrogen peak intensity is due to the cleavage of amide functional groups caused by hydrolysis or photolysis.¹⁹ However, XPS results show that nitrogen is only physisorbed. The concentration of the numerous oxidation products, other than for hydroperoxides and alcohols, are ordered according to the following decreasing order: carboxylic acids

> ketones > esters > peracids, peresters > alkenes. These results are in agreement with those obtained by other authors who used chemical reactions to attain this goal.^{4,6,7}

The intensity of the band centered at 842 cm^{-1} , which is attributed to the C—C vibration, is merely affected by the aging phenomenon and hence it can be used as a reference band to normalize the carbonyl absorption band and to compare the aged samples.⁴ On the contrary, the intensity of the methylene group shows an interesting alteration during oxidation. Actually, as the intensity of the methylene decreases, that of the carbonyl increases, thus confirming that the oxidative attack preferentially occurs on the methylene group. Consequently, the steps of the mechanism proposed earlier for the same aging of the PP samples studied by XPS² remain the same, except that the site of oxidative attack is the secondary carbon as opposed to the tertiary carbon. Therefore, the most probable mechanism is the following one:

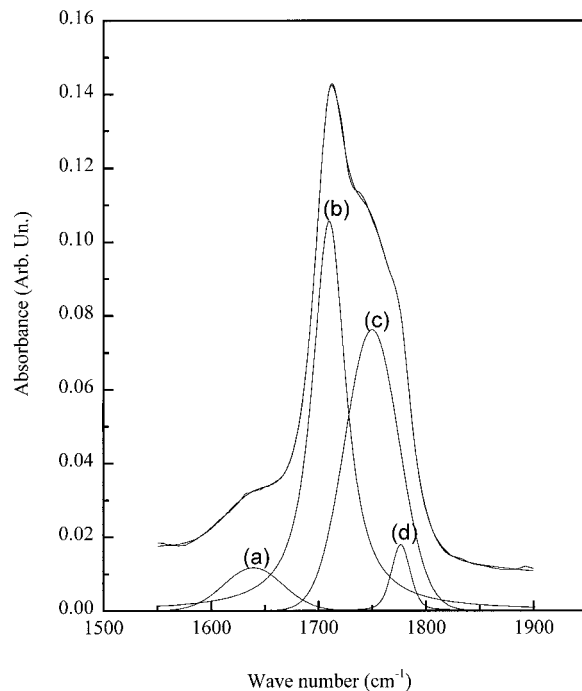
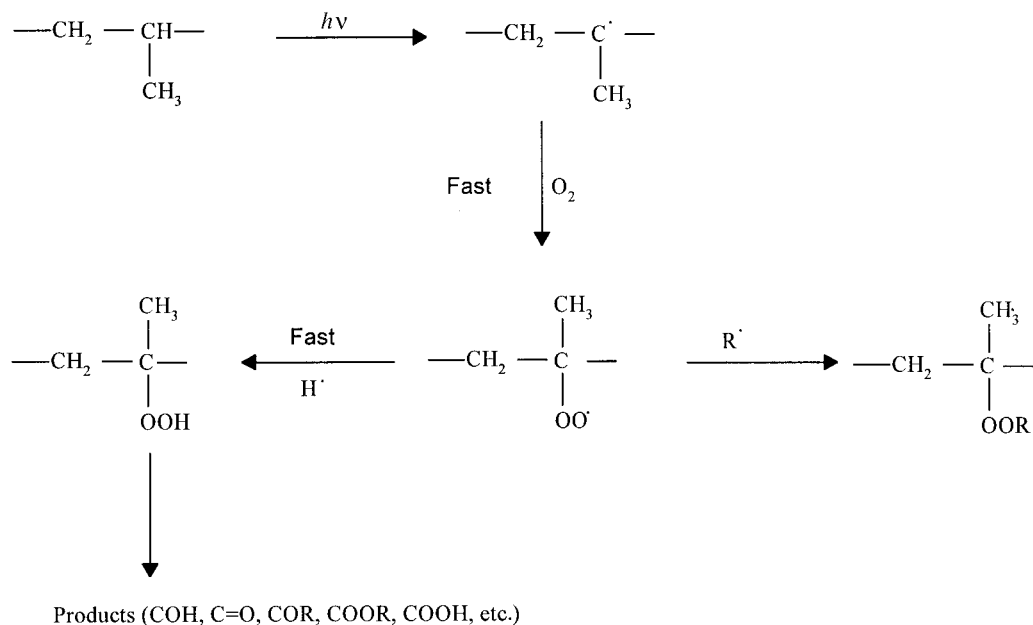
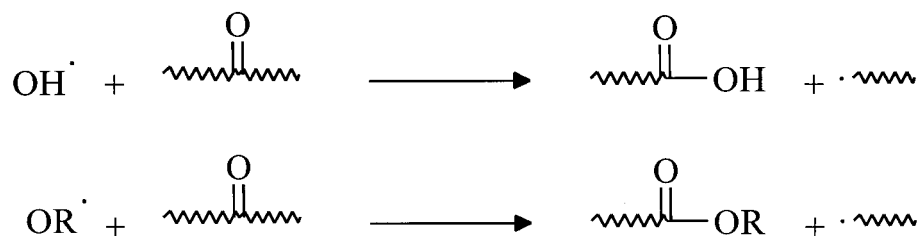


Figure 7 IR spectra of the polypropylene sample aged under an ambient atmosphere and ambient light, which shows a four-peak deconvolution: (a) C=C at 1640 cm^{-1} , (b) the acid dimeric form and/or ketone or aldehyde at 1710 cm^{-1} , (c) a free acid and/or ester at 1751 cm^{-1} , and (d) a peracid and/or perester at 1777 cm^{-1} .



Henceforth, IR spectroscopy allowed us to clearly determine the site of oxidative attack, as corroborated by our XPS results.² It permitted the detection of oxygen in the new sample, even though it was present in trace amounts. It also aided in visualizing the increasing degree of oxidation

(Fig. 4). However, the closeness of the absorption bands in the complicated mixture of aldehydes, ketones, esters, acids, peresters, and peracids, along with the difficulties of differentiating between hydroperoxides and alcohols, rendered the qualitative analyses more difficult.



CONCLUSION

The data obtained via IR spectroscopy were useful in determining the structural modifications brought about by aging of a commercial PP sample. Indeed, three types of PP samples were analyzed: the first sample was absolutely new, the second had been exposed to an ambient atmosphere but sheltered from ambient light, while the third was exposed to both an ambient atmosphere and ambient light.

The IR spectrum of the new sample (Fig. 1) reveals the presence of oxygen, which is incorpo-

rated into the polymeric chain via single chemical bonds, and indicates that the commercial sample is isotactic. After aging under an ambient atmosphere but hidden from the sun (Fig. 2), the spectrum shows the presence of a carbonyl group. The deconvolution of this peak indicates the presence of a complicated mixture of oxidation products: ketones conjugated to alkenes, nonconjugated ketones, aldehydes, esters, acids (carboxylic acids can exist as stable dimers, which absorb at 1710 cm^{-1} , or as free acids,²⁰ which absorb at 1755 cm^{-1}), peresters, and peracids. The decreased in-

tensity of methylene confirms that it is the favorable oxidation site. The IR spectrum of the third sample, aged and exposed to ambient light, is similar to the spectrum for the second sample. However, the intensity of the carbonyl group is greater for the third sample, and the deconvolution of this band shows the absence of the conjugated ketone. Also, the intensity of the numerous oxidation products is increased. All these factors thus imply that ambient light favors the oxidation of PP.

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