Photo- and Thermal-Oxidation of the Nonwoven Polypropylene Fabric Studied by FT-IR Photoacoustic Spectroscopy

CHARLES Q. YANG[1,*] and LINETTE K. MARTIN[2]

[1]Department of Textiles, Merchandising and Interiors, The University of Georgia, Athens, Georgia 30602 and
[2]Department of Chemistry, Marshall University, Huntington, West Virginia 25701

SYNOPSIS

The photo- and thermal-oxidation of a nonwoven polypropylene fabric was investigated using Fourier transform infrared photoacoustic spectroscopy (FT-IR/PAS). The infrared spectroscopic data indicate that alcohol, peroxide, aldehyde, ketone, carboxylic acid, and anhydride were formed as the products of the thermal oxidation and photooxidation of the polypropylene fabric. Ester was also formed during the thermal oxidation process. The thermal oxidation was accelerated after an initiation period. It was found that thermal oxidation occurred homogeneously between the surfaces of the fabric and its bulk. For the polypropylene fabric irradiated by ultraviolet (UV) radiation, however, the highest degree of oxidation occurred in the surface of the fabric facing the UV radiation source. It was also found that the UV radiation at 254 nm caused photooxidation of polypropylene. No photooxidation was observed in the fabric exposed to the UV radiation at 350 nm under the same conditions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, polyolefin have been used in the production of nonwoven fabrics for various industrial and consumer applications. The total amount of nonwovens produced in the United States was 272 million pounds in 1991, with an annual growth rate of 17%.[1] Polypropylene is the leading polymer used in the nonwoven industry. More than half of all nonwoven fabric consumption occurs in disposable products including sanitary, health care, and industrial or institutional items.[2] The extensive use of disposable polyolefin nonwoven items has caused increasing concern over their impact on the environment, because neither polyethylene nor polypropylene are environmentally degradable. The manufacturers often make those nonwovens even less degradable by adding antioxidants to them. Thus, it is important to understand the degradation of nonwoven polyolefin fabrics under various conditions. Those conditions, which include heat and UV radiation, occur in the production and use of nonwoven items as well as their disposal.

The fundamental process of degradation and stabilization of polyolefins has been extensively studied.[3–7] Infrared spectroscopy has been one of the commonly used analytical techniques for the studies of polyolefin degradation and stabilization.[8–10] In the past, the infrared spectroscopy studies were carried out using transmission or attenuated total reflection (ATR) techniques on polyolefin films. The oxidation of polyolefin fabrics or fibers has not been investigated.

In this research, Fourier transform infrared photoacoustic spectroscopy (FT-IR/PAS) was used for investigating the thermal and photo degradation of a melt-blown nonwoven polypropylene fabric. In a PAS experiment, it is not the transmitted or reflected IR radiation, but the acoustic signals generated by the absorbed radiation, that are detected and then Fourier transformed to yield a single-beam spectrum. Consequently, opaque samples can be analyzed without any difficulties. Samples are not altered during a process of analysis. A PA-IR spectrum

---

resembles a transmission spectrum and does not suffer band distortion or band frequency shift, which can be frequently found in diffuse reflectance IR spectra.[11]

FT-IR/PAS can also be used as a near-surface analytical method to investigate textile samples. In our previous research, FT-IR/PAS has demonstrated the capability of differentiating the near surfaces of a fabric or a fiber from its bulk.[11-15] Here, FT-IR/PAS was used to identify the photo- and thermal oxidation products and to determine the distribution of those oxidation products between the surfaces of a nonwoven polypropylene fabric and its bulk.

EXPERIMENTAL

Instrumentation

A Nicolet 20DXB FT-IR spectrometer with an MTEC Model 100 PA cell was used to collect all the spectra. Carbon black was used as a reference material, and helium was used as the purging and conducting gas in the PA cell. The number of scans was 500 for each spectrum. The mirror velocity was 0.139 cm/s, no base line correction or smoothing function was used. The carbonyl band intensity and the hydroxyl band intensity were normalized against the band at 2922 cm^{-1}, which is associated with the asymmetric stretching of methylene in polypropylene molecules.

Fabric Treatment

A melt-blown nonwoven polypropylene fabric (1.5 oz/yd^2, 800 meltflow rate) was used in this research. The polypropylene fabric contains a phenolic antioxidant. The polypropylene fabric was heated in an oven. The temperature variation was ±3°C. The same fabric was also placed beneath an ozone-free 254-nm ultraviolet light at room temperature. The lamp used was a Sylvania GTE germicidal lamp. The radiation intensity at a distance of 2.5 cm from the bare tube is approximately 18 μW/cm^2. Powder samples were obtained by grinding the fabric samples in a Wiley mill to pass a 40-mesh screen. The mean thickness of the polypropylene fabric is 0.60 mm as determined by an electronic Ames Gauge.

The oxidized polypropylene fabric was treated with various chemicals for the purpose of identifying the oxidation products.

Treatment with NaOH: A fabric sample was first treated with a 0.25 M NaOH solution in ethanol at room temperature for 5 min. The sample was finally rinsed with ethanol and dried.

Treatment with sodium borohydride: A fabric sample was placed in a 1.0 M sodium borohydride solution in ethanol and brought to reflux. The reflux was continued for 1 h. The sample was then washed with ethanol, and finally treated with a 0.1 M NaOH solution in ethanol for the purpose of converting all carboxyl to carboxylate.

Saponification: A fabric sample was treated with a 0.25 M NaOH solution in ethanol at 50°C for 3 h. The sample was finally rinsed with ethanol and dried.

RESULTS AND DISCUSSION

Thermal Oxidation

The PA-IR spectra of the nonwoven polypropylene fabric heated at 120°C for different times are presented in Figure 1. The IR spectroscopy data indicate that thermal oxidation did not occur in the polypropylene fabric even after the fabric was exposed to heat for 600 h [Fig. 1(F)]. The phenolic antioxidant contained in the polypropylene fiber was effective in prohibiting the thermal oxidation process.

The polypropylene fabric was extracted by methylene chloride for 2.5 h to remove the antioxidant, and then heated at 120°C. The IR spectrum of the polypropylene fabric extracted and heated for 30 h shows a broad band in the 3350–3420 cm^{-1} frequency region, which is due to the stretching mode of hydrogen-bonded hydroxyl [Fig. 2(B)]. This indicates that alcohol/peroxide was formed during the thermal oxidation process. A weak carbonyl band at 1708 cm^{-1} is also seen in Figure 2(B). The carbonyl band increased its intensity and broadened when the exposure time was increased from 30 to 42 h [Fig. 2(B–F)]. The intensity of the hydroxyl band at 3424 cm^{-1} also increased during the same period [Fig. 2(B–F)].

The intensities of the carbonyl band and the hydroxyl band for different exposure times are presented in Figures 3 and 4. The thermal oxidation of the polypropylene fabric was slow during the first 30 h and little thermal oxidation was observed in the fabric. It appears that the thermal oxidation had an initiation period. The oxidation was accelerated during the next 12 h as shown by a drastic increase in both carbonyl and hydroxyl band intensities. After the fabric was exposed for 42 h, a further increase in exposure time only resulted in a slight increase in both the carbonyl band intensity and the hydroxyl band intensity.
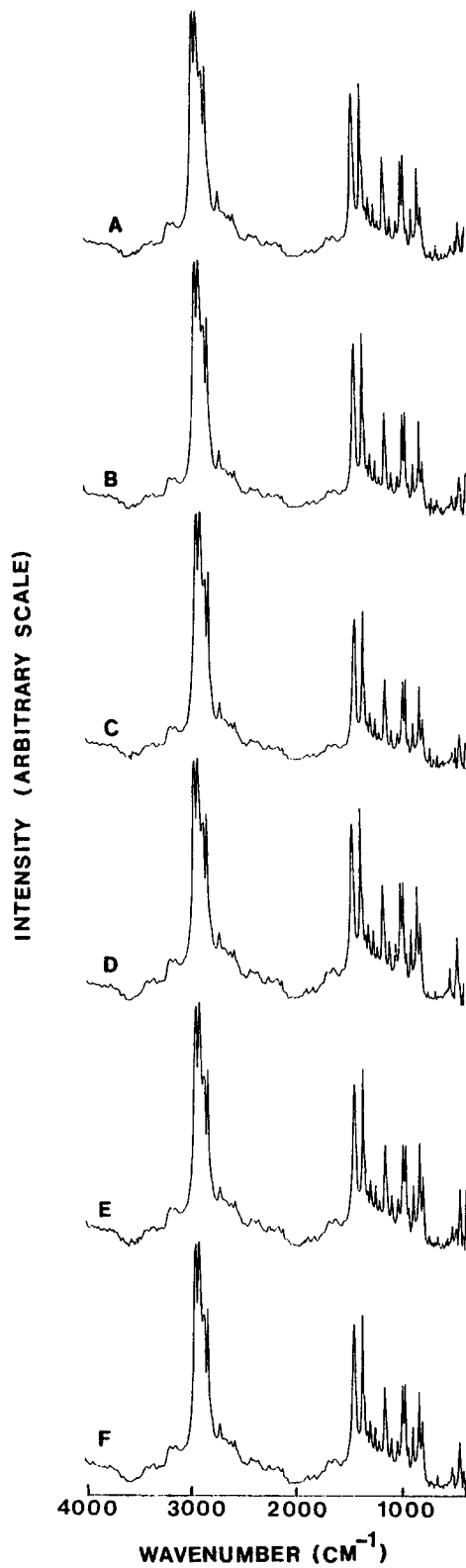
Figure 1 PA-IR spectra of the polypropylene fabric heated at 120°C for different times (h): (A) 0; (B) 120; (C) 240; (D) 360; (E) 480; (F) 600.
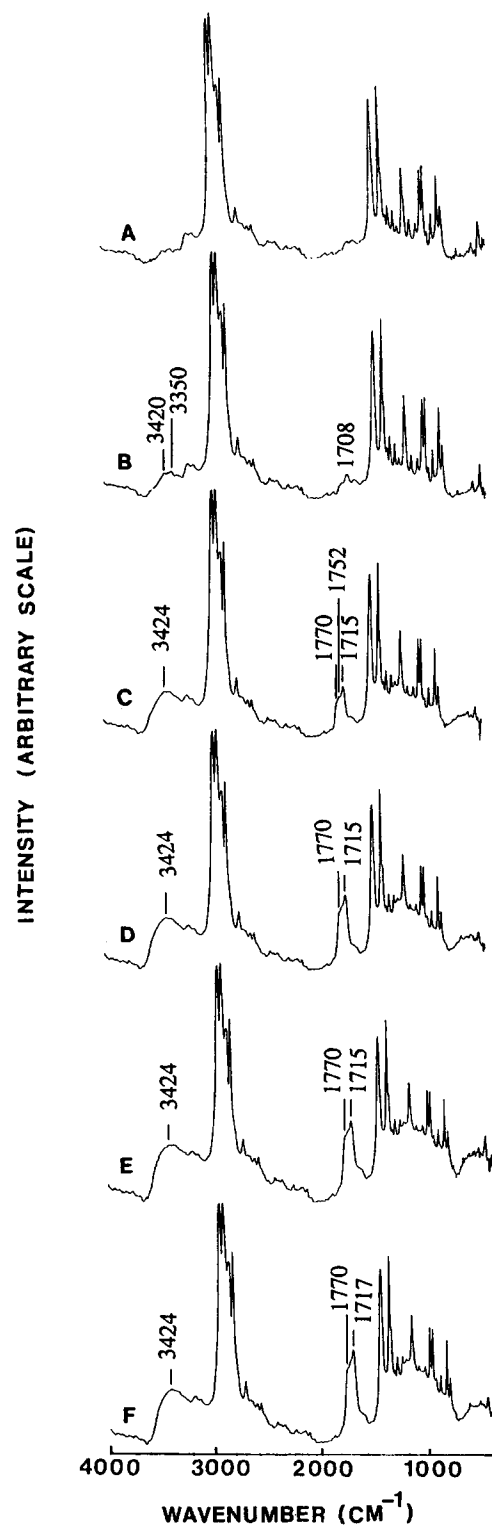
Figure 2 PA-IR spectra of the polypropylene fabric first extracted with methylene chloride, then heated at 120°C for different times (h): (A) 0; (B) 30; (C) 32; (D) 34; (E) 36; (F) 42.
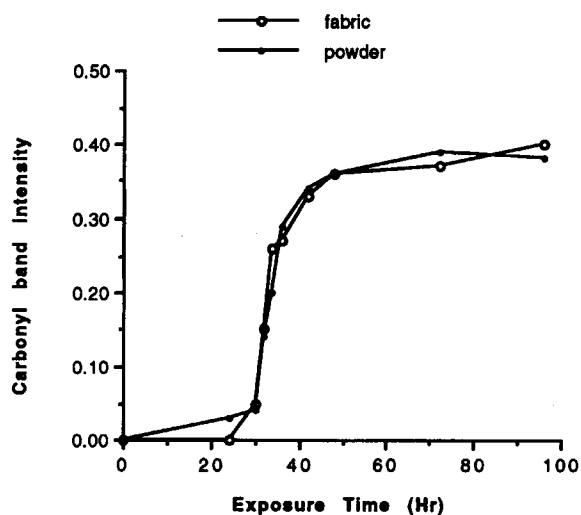
Figure 3 The carbonyl band intensity of the polypropylene fabric heated at 120° for different times.

In order to determine the nature of the oxidation products, the polypropylene fabric extracted and then heated at 120°C for 32 h was treated with a 0.25M NaOH solution for 5 min at room temperature. The PA-IR spectrum of the fabric thus treated shows that the intensity of the carbonyl band at 1715 cm^{-1} was reduced while a new band at 1617 cm^{-1} due to the asymmetric stretching mode of carboxylate carbonyl developed [Fig. 5(B)]. Treatment of the fabric with NaOH converted carboxylic acid to carboxylate. A decrease in the intensity of the carbonyl band at 1715 cm^{-1} and development of the
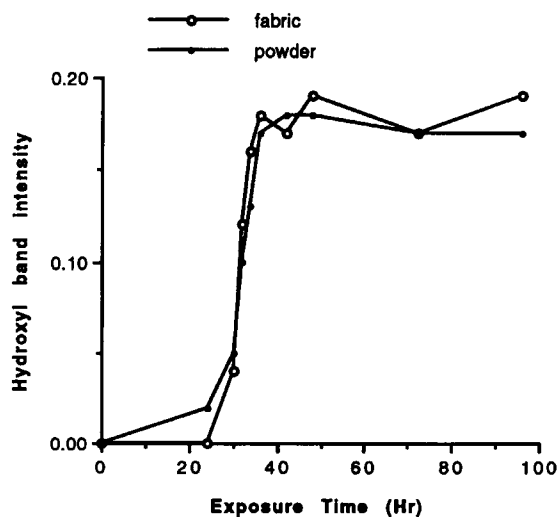

Figure 4 The hydroxyl band intensity of the polypropylene fabric heated at 120°C for different times.
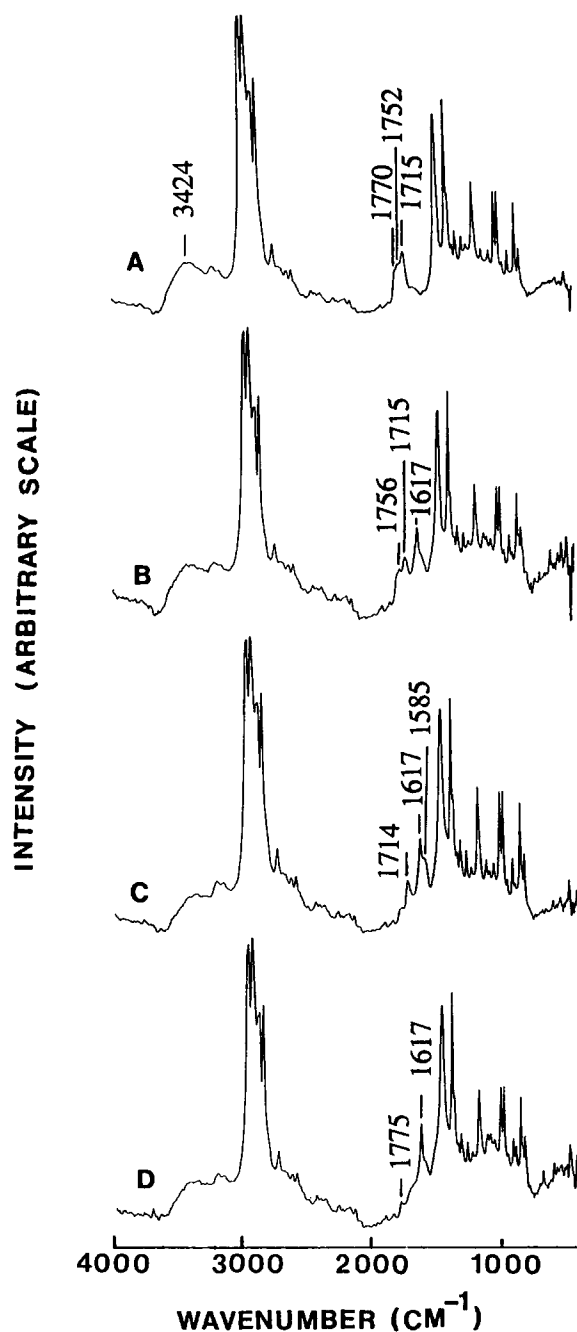

Figure 5 PA-IR spectra of the polypropylene fabric extracted with methylene chloride and heated at 120°C for 32 h: (A) no treatment; (B) treated with NaOH at room temperature for 5 min; (C) treated with NaOH at 50°C for 3 h; (D) the fabric described in C, treated with sodium borohydride.

carboxylate carbonyl band at 1617 cm^{-1} in Figure 5(B) indicate that the 1715 cm^{-1} band in Figure 5(A) is partially contributed by carboxyl carbonyl.

The same fabric was also treated in a 0.25M

NaOH solution at 50°C for 3 h. The intensity of the carbonyl band at 1715 cm^{-1} is further reduced after the treatment, whereas a shoulder at 1585 cm^{-1} emerges in the spectrum [Fig. 5(C)]. The IR spectroscopy data reveal that saponification occurred when the fabric was treated with the NaOH solution at 50°C for 3 h. The band at 1715 cm^{-1} in Figure 5(B) is partially contributed by hydrogen-bonded ester carbonyl, whereas the band at 1585 cm^{-1} is due to the carboxylate carbonyl. The further reduction of the 1715 cm^{-1} band intensity in Figure 5(C) is a result of transformation of ester to carboxylate.

A shoulder at 1752 cm^{-1} is seen in Figure 5(A). Figure 5(B) also shows a carbonyl band at 1756 cm^{-1}. This band completely disappears after the fabric was treated with the NaOH solution at 50°C for 3 h [Fig. 5(C)]. The band around 1752–1756 cm^{-1} is likely associated with the carbonyl of a non-cyclic anhydride, which was converted to carboxylate after the treatment by NaOH for 3 h.

The nonwoven polypropylene fabric described above was treated with a 1.0 M sodium borohydride solution at reflex. The carbonyl band at 1714 cm^{-1} shown in Figure 5(C) disappears completely in the IR spectrum of the fabric thus treated [Fig. 5(D)]. Because sodium borohydride reduces aldehyde and ketone to primary and secondary alcohols, the IR spectroscopy data presented here indicate that the band at 1714 cm^{-1} in Figure 5(C) is due to carbonyls of ketone and aldehyde. Therefore, the carbonyl band at 1715 cm^{-1} in Figure 5(A) is partially attributed to aldehyde and ketone.

A shoulder at 1770 cm^{-1} is seen in the spectra of the oxidized polypropylene fabric [Fig. 2(C–F)]. A weak band at 1775 cm^{-1} is also shown in Figure 5(D). The band around 1770 cm^{-1} is likely due to the symmetric stretching mode of cyclic anhydride carbonyl. The influence of ring strain induces a shift of the carbonyl bands to a higher frequency.[16] The symmetric stretching frequency of strained cyclic anhydride, such as succinic anhydride, is around 1778–1780 cm^{-1}.[16] A five-member cyclic anhydride is formed as the dehydration product of two adjacent carboxyl groups.[17]

The bands in the 1715–1770 cm^{-1} region in Figure 5(A) are due to various carbonyls, that are hydrogen-bonded by hydroxyl or carboxyl formed during the oxidation process. Those bands are broadened by the hydrogen bonding; therefore they overlap each other to form a broad band as shown in Figure 2. The formation of the actual oxidation products are possibly more complicated than what are indicated here.

The broad band at 3424 cm^{-1} in Figure 2 due to the hydroxyl stretching mode is contributed by hydrogen-bonded hydroxyl of alcohol and peroxide as well as hydrogen-bonded hydroxyl of carboxylic acid. The thermal oxidation products of the nonwoven polypropylene fabric is summarized in Table I.

The distribution of the oxidation products between the surfaces of the polypropylene fabric and its interior was also investigated using FT-IR/PAS. The polypropylene fabric extracted and then heated at 120°C for different times were ground into powders. The intensities of the hydroxyl band and the carbonyl band in the IR spectra of the powder samples are presented in Figures 3 and 4. The intensities of these two bands in the spectra of the fabric samples appear to be similar to those in the spectra of the powder samples.

In a PAS experiment, modulated IR radiation is first absorbed by a sample. The absorbed IR radiation is converted to heat. When the heat propagates to the sample's surface, and subsequently into the gas within a PA cell, it causes pressure variation and generates an acoustic signal. When a sample's thickness is larger than the thermal diffusion length, only the heat generated within the first thermal diffusion length from the sample's surface can propagate to the surface and generate photoacoustic signals.[18] Because the thermal diffusion length of polypropylene in the mid-IR region is in the range of a few micrometers, the PA-IR spectrum of a fabric sample represents a few micrometers' near surface of the fabric. When the fabric is ground into a powder, the near surface and the bulk are mixed. Because the thickness of the polypropylene fabric is approximately 600 micrometers, the PA-IR spectrum of the powder sample represents mainly the bulk. The similarity between the hydroxyl and carbonyl band intensities in the spectra of the fabric samples and those in the spectra of the powder samples demonstrate that the thermal oxidation was homoge-

Table I   Thermal Oxidation Products of Nonwoven Polypropylene Fabric

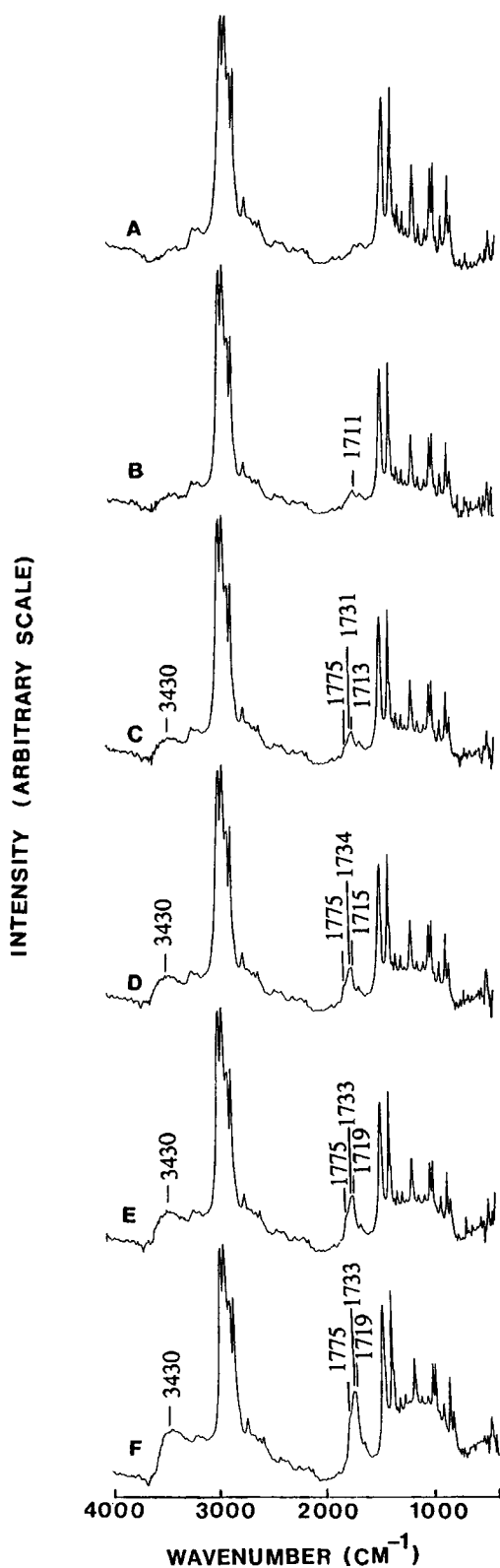| Oxidation Products	IR Band Frequency (cm^{-1})
Alcohol and peroxide hydroxyl	~3424
Ketone and aldehyde carbonyl	1708–1715
Carboxyl carbonyl	1715–1717
Ester carbonyl	~1715
Anhydride carbonyl	1756, 1770–1775

Figure 6 PA-IR spectra of the front surfaces of the polypropylene fabric exposed to ultraviolet radiation at 254 nm for different times (h): (A) 0; (B) 48; (C) 72; (D) 96; (E) 120; (F) 168.

neous between the surface and the bulk of the polypropylene fabric.

Photooxidation

The PA-IR spectra of the front surface of the polypropylene fabric exposed to UV radiation at 254 nm for different times are presented in Figure 6. A weak carbonyl band at 1711 cm^{-1} and a weak hydroxyl band around 3430 cm^{-1} developed when the fabric was exposed to the UV radiation for 48 h [Fig. 6(B)]. The carbonyl band was broadened with the development of a new component at 1731 cm^{-1} and a shoulder at 1775 cm^{-1} when the fabric was exposed to the UV radiation for 72 h [Fig. 6(C)]. The hydroxyl band at 3430 cm^{-1} was also broadened with an increased intensity in Figure 6(C). The formation of the hydroxyl and the carbonyl appeared to be simultaneous during the photooxidation process. An increase in exposure time caused an increase in the intensities of both the carbonyl band and the hydroxyl band as shown in Figure 6.

The intensities of the carbonyl band and the hydroxyl band of the exposed polypropylene fabric are shown in Figures 7 and 8. The IR spectroscopy data indicate a gradual increase in both the carbonyl band intensity and the hydroxyl band intensity as the exposure time is increased. This is obviously different from the thermal oxidation, which was accelerated after a 30-h initiation period (Figs. 3, 4).

The photooxidation products of the polypropylene fabric were identified using IR spectroscopy. The polypropylene fabric exposed to the UV radiation
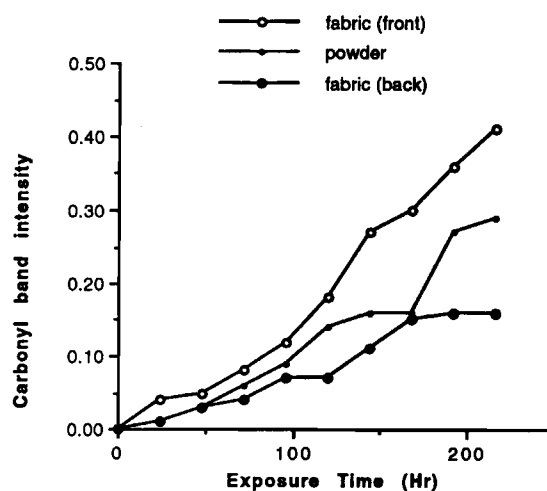

Figure 7 The carbonyl band intensity of the polypropylene fabric exposed to UV radiation at 254 nm for different times.
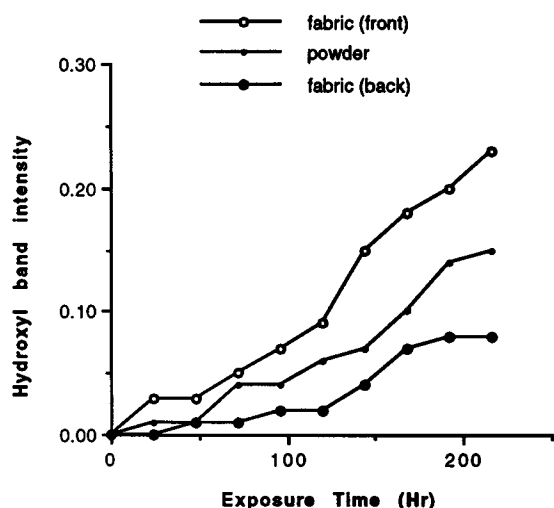
Figure 8 The hydroxyl band intensity of the polypropylene fabric exposed to UV radiation at 254 nm for different times.

at 254 nm for 72 h was treated with a 0.25 M NaOH solution for 5 min at room temperature. The PA-IR spectrum of the polypropylene fabric thus treated [Figure 9(B)] demonstrates that the intensity of the carbonyl band at 1713 cm^{-1} was reduced whereas a new band at 1619 cm^{-1} developed. The band at 1619 cm^{-1} in Figure 9(B) is associated with the asymmetric stretching mode of carboxylate carbonyl. The reduction in the 1713 cm^{-1} carbonyl band intensity was a result of conversion of carboxyl to carboxylate by the NaOH solution. Therefore, it can be concluded that carboxyl is one of the oxidation products. No further reduction in the 1712 cm^{-1} band intensity was observed when the fabric was treated with the same NaOH solution at 50°C for an extended period of time. It was unlikely that a substantial quantity of ester formed during the photooxidation process.

The polypropylene fabric described above was treated with a 1.0 M sodium borohydride solution at reflex for 1 h. The carbonyl band at 1712 cm^{-1} in Figure 9(B) disappears completely, whereas the carboxylate carbonyl band at 1616 cm^{-1} remains in the spectrum of the polypropylene fabric thus treated [Fig. 9(C)]. It can be concluded that the carbonyl band at 1712 cm^{-1} in Figure 9(B) is associated with ketone and aldehyde. Sodium borohydride reduced the ketone and aldehyde to secondary and primary alcohols. A band at 3690 cm^{-1} due to the stretching mode of isolated hydroxyl groups of alcohols was also observed in the spectrum of the sodium borohydride-treated fabric [Fig. 9(C)].

The shoulder at 1778 cm^{-1} in Figures 9(A, B),

and the weak band at 1778 cm^{-1} in Figure 9(C) are due to the asymmetric stretching mode of anhydride carbonyl. The anhydride is likely a five-member cyclic anhydride formed as the dehydration product of two adjacent carboxyl groups. As discussed above, all the carbonyl bands observed here are broad and overlapped each other because the carbonyls are hydrogen-bonded to hydroxyl or carboxyl formed during the photooxidation process.

The broad band at 3430 cm^{-1} in Figure 6 can be assigned to the stretching mode of the hydrogen-bonded hydroxyl of alcohol and peroxide. The photooxidation products of the nonwoven polypropylene fabric is summarized in Table II.

Also presented in Figures 7 and 8 are the intensities of the carbonyl band and the hydroxyl band
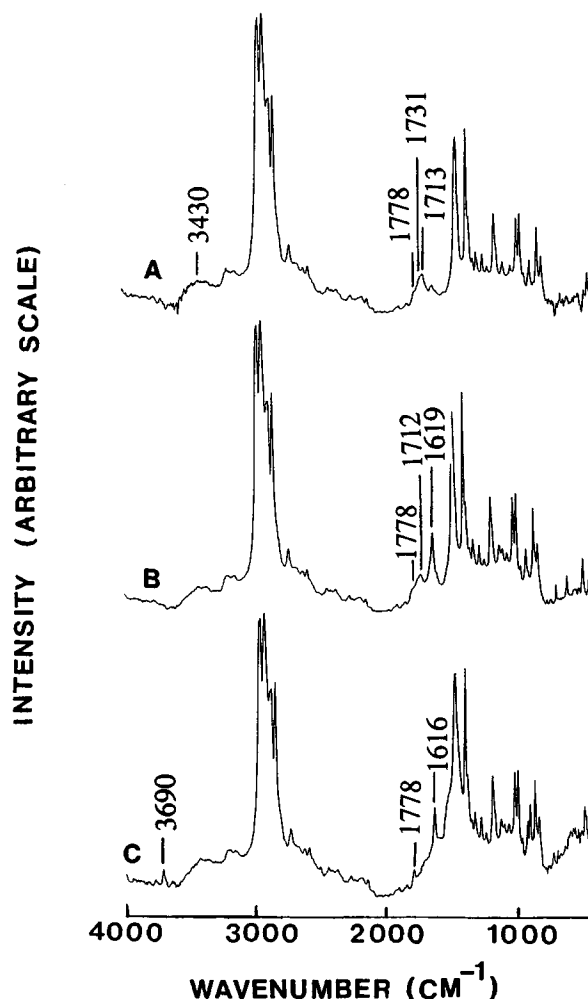

Figure 9 PA-IR spectra of the polypropylene fabric exposed to UV radiation at 254 nm for 72 h: (A) no treatment; (B) treated with NaOH at room temperature for 5 min; (C) the fabric described in B, treated with sodium borohydride.

Table II   Photooxidation Products of Nonwoven Polypropylene Fabric

Oxidation Products	IR Band Frequency (cm^{-1})
Alcohol and peroxide hydroxyl	~3430
Ketone and aldehyde carbonyl	1711–1719
Carboxyl carbonyl	1713–1731
Anhydride carbonyl	1775–1778

in the PA-IR spectra of the powders and the back surfaces of the polypropylene fabric exposed to the UV radiation for different times. Figures 7 and 8 indicate that the intensities of the carbonyl band and the hydroxyl band in the spectra of the powder sample and the back surface gradually increased as the exposure time was increased. The change in the carbonyl band intensity and the hydroxyl band intensity follow the same trend for the front surface, the powder and the back surface of the polypropylene fabric. However, the carbonyl and hydroxyl band intensities for the three types of samples are different. The intensities of the two bands for the powders are lower than those for the front surfaces of the polypropylene fabric. They are further reduced for the back surfaces of the fabric.

As we discussed above, a spectrum of a fabric represents the near surface of the fabric whereas a spectrum of a powder of the fabric represents the bulk of the fabric. The differences in the carbonyl band and hydroxyl band intensities among the spectra of the front surface, powder, and back surface of the polypropylene fabric shown in Figures 7 and 8 indicate an inhomogeneous distribution of the photooxidation products between the surfaces and the bulk of the polypropylene fabric.

The IR spectroscopy data presented here demonstrate that the UV radiation was able to penetrate through the polypropylene fabric and caused photooxidation in the bulk of the fabric. The highest degree of photooxidation occurred in the surface of the fabric facing the UV radiation source, whereas the lowest degree of photooxidation occurred in the back surface of the fabric. The changes in the degree of photooxidation across the fabric was probably due to changes in the intensity of the UV radiation in the fabric. While the UV radiation was penetrating through the fabric, its intensity decreased due to scattering and absorption. A similar phenomenon was also observed in the photooxidation of cotton fabric.[19]

In the past, all the studies of the photooxidation

of polyolefin was carried out on films. Furneaux and co-workers[20] reported that the carbonyl concentration was the greatest on both the front and back surfaces of a polyethylene film exposed to UV radiation, and that the carbonyl concentration fell off toward the center. As a result, the photooxidation in the back half of the film was nearly a mirror image of the front half. The lower degree of photooxidation in the bulk of a film was evidently due to insufficient oxygen diffusion into the interior of the film. The amount of oxygen supply from the surfaces of the film to the interior was lower than that around both surfaces of the film. This reduced the degree of photooxidation in the bulk of the film.

The melt-blown nonwoven fabric used in this research has an open structure, therefore the oxygen supply is abundant for the photooxidation of the polypropylene fibers in the entire fabric. Oxygen diffusion is no longer a factor in limiting the degree of oxidation in the bulk of the nonwoven fabric. Fibers have extremely high surface-to-volume ratio, thus causing light scattering and reducing the intensity of the UV radiation when UV radiation is penetrating from the front surface toward the back surface. As a result, the degree of photooxidation decreases from the front surface toward the back surface of the polypropylene fabric.

The polypropylene fabric was extracted by methylene chloride to remove the antioxidant. The extracted polypropylene nonwoven fabric was exposed to the UV radiation at 254 nm for the same time periods as those for the polypropylene fabric not extracted. The PA-IR spectra of the extracted and exposed polypropylene fabric appear to be identical to Figure 6. It indicates that the presence of the antioxidant had no effect on the photooxidation of polypropylene.

The nonwoven polypropylene fabric was also exposed to the UV radiation at 350 nm for different times. The PA-IR spectrum of the polypropylene fabric exposed to the radiation for 216 h showed no formation of either carbonyl or hydroxyl.

CONCLUSIONS

1. Alcohol, peroxide, ketone, aldehyde, carboxylic acid, ester, and anhydride were formed as the thermal oxidation products of the nonwoven polypropylene fabric. The thermal oxidation was accelerated after an initiation period. The thermal oxidation products were homogeneously distributed between the surfaces and the bulk of the polypropylene fabric.

The thermal oxidation was suppressed by the phenolic antioxidant.

2. Alcohol, peroxide, ketone, aldehyde, carboxylic acid, and anhydride were formed as the photooxidation products of the nonwoven polypropylene fabric. The highest degree of photooxidation occurred in the front surface of the fabric facing the UV radiation source, whereas the lowest degree of photooxidation occurred in the back surface of the fabric.

3. The UV radiation at 254 nm caused photooxidation of the nonwoven polypropylene fabric. However, no photooxidation was observed in the fabric exposed to the UV radiation at 350 nm under the same conditions.

REFERENCES

1. D. Harrison, *Nonwoven Industry*, **23**, 18 (1992).
2. N. D. Sharma and R. Raman, *Textile Asia*, **August**, 84 (1988).
3. J. F. McKellar and N. S. Allen, *Photochemistry of Man-made Polymers*, p. 31, Elsevier Applied Science Publishers Ltd., London, pp. 1979.
4. B. Ranby and J. F. Rabek, *Photodegradation, Photooxidation and Photostabilization of Polymers*, Wiley, London, 1975.
5. A. Garton, D. J. Carlsson, and D. M. Wiles, *Development in Polymer Photochemistry*, p. 93 N. S. Allen, Ed., Elsevier Applied Science Publishers Ltd., London, 1980.
6. N. S. Allen, *Degradation and Stabilization of Polyolefins*, Applied Science Publishers, London, 1983.
7. N. Grassie and G. Scott, *Polymer Degradation and Stabilization*, p. 68, Cambridge University Press, Cambridge, 1985.
8. D. I. Bower and W. F. Maddams, *The Vibration Spectroscopy of Polymers*, p. 223. Cambridge University Press, Cambridge, 1989.
9. W. D. Domke and H. Steinke, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 2701 (1986).
10. P. Blais, D. J. Carlson, and D. M. Wiles, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 1077 (1972).
11. C. Q. Yang, *Appl. Spectrosc.*, **45**, 102 (1991).
12. C. Q. Yang, R. R. Bresee, and W. G. Fateley, *Appl. Spectrosc.*, **41**, 889 (1987).
13. C. Q. Yang, T. A. Perenich, and W. G. Fateley, *Textile Res. J.*, **59**, 562 (1989).
14. C. Q. Yang, R. R. Bresee, and W. G. Fateley, *Appl. Spectros.*, **44**, 1035 (1990).
15. C. Q. Yang, *Ind. Eng. Chem. Res.*, **31**, 617 (1992).
16. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 3rd ed., p. 144, Chapman and Hall, London, 1975.
17. C. Q. Yang, *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 1187 (1993).
18. A. Rosencweig, *Photoacoustics and Photoacoustic Spectroscopy*, p. 93, Wiley, New York, 1980.
19. C. Q. Yang and J. M. Freeman, *Appl. Spectrosc.*, **45**, 1695 (1991).
20. G. C. Furneaux, K. J. Ledbury, and A. Davis, *Polym. Degrad. Stability*, **3**, 431 (1880).