Photoaging and Stabilization of Rigid PVC/Wood-Fiber Composites

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ABSTRACT: Ultraviolet (UV) weathering performance of unpigmented and rutile titanium dioxide pigmented rigid polyvinyl chloride (PVC)/wood-fiber composites has been studied. The composite samples were manufactured by dry-blending PVC, wood fibers, and other processing additives in a high-intensity mixer. The dry-blended compounds were extruded and compression molded into panel samples. The manufactured samples were artificially weathered using laboratory accelerated UV tests. Composite samples were exposed to 340-nm fluorescent UV lamps and assessed every 200 h, for a total of 1200 h of accelerated weathering. Each assessment consisted of a visual examination of surface roughness or erosion, a contact angle measurement, a FTIR collection, and a color measurement. The experimental results indicated that wood fibers are effective sensitizers and that their incorporation into a rigid PVC matrix has a deleterious effect on the ability of the matrix to resist degradation caused ultraviolet irradiation. The light stability of these composites could be improved quite efficiently with the addition of rutile titanium dioxide photoactive pigment during formulation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1943–1950, 2001

Key words: ultraviolet degradation; PVC/wood-fiber composites; FTIR; contact angle; discoloration; light stabilizer

INTRODUCTION

The use of wood fibers as fillers and/or reinforcers for flexible and rigid polyvinyl chloride (PVC) products has grown extremely rapidly during the past years. Characterized by high specific stiffness and strength, wood fibers offer a number of advantages over the currently used reinforcing inorganic materials (e.g., glass fibers, calcium carbonate, talc, mica) in terms of cost on a unit-volume basis, flexibility during processing, and stiffness.[1–7] In spite of these advantages, a considerable problem for the outdoor applications of PVC/wood-fiber composites is that terrestrial sunlight can cause photodegradation. This degradation is mainly due to the high susceptibility of both the PVC matrix[8–18] and wood fibers[19–21] to photodegradation when exposed to such factors as long-term solar ultraviolet (UV) radiation, rain, snow, and pollutants. Photodegradation results in a serious deterioration in mechanical properties[8,9,17] and color change[8–12] of the material during service life and is of special concern for the use of these composites in outdoor applications.

The mechanism of photochemical degradation of PVC products has been thoroughly investigated during the past few decades.[8–18] It is generally

accepted that the photodegradation of PVC proceeds primarily by a radical-type mechanism. When a PVC sample is exposed to sunlight or artificial UV radiation, discoloration occurs rapidly due to the formation of alkene or polyene linkages.[8,9] Simultaneously, large amounts of hydrogen chloride evolve (dehydrochlorination) while the polymer chains undergo scission and crosslinking,[8,9,15,16] with the expected deleterious effects on the mechanical properties.[17] This degradation is substantially accelerated by the presence of chromophore materials (impurities) such as carbonyl and hydroperoxide groups within the polymer chain or on side groups. These chromophoric groups contaminate commercial PVC and are able to initiate the dehydrochlorination reaction because they effectively absorb the incident light.[8,9]

Similarly, wood exposed outdoors undergoes photochemical degradation. Research has shown that weathering of wood is a process that is confined to the surface of the wood, involving photo-induced breakdown of lignin to water soluble reaction products (a loss of lignin). This leads to the generation of chromophoric functional groups such as carbonyls, carboxylic acids, quinones, and hydroperoxy radicals.[19,20]

Although considerable information is available on the mechanisms of photodegradation of either PVC[8–18] or wood,[19–21] previous research has not extensively examined the outdoor performance of wood fiber-filled rigid PVC composites. The objective of the present study is to investigate the photodegradation and stabilization of rigid PVC/wood-fiber composites exposed to accelerated UV weathering tests.

EXPERIMENTAL

Materials

The polymer matrix used in this study was PVC (K value = 57) supplied by Oxyvinyls. Calcium stearate (Synpro, Ferro) and household paraffin wax (Gulf Wax) were used as lubricants. Liquid tin stabilizer (PlastiStab 2808, OMG Americas) was used as heat stabilizer. Rutile titanium dioxide (TiO_2 Kemira 460, Kemira Pigments) was used as photoactive pigment. Other processing aids (Paraloid K-120 and Paraloid K-175, Rohm and Haas) were also used as ingredients in the formulations to facilitate processing. Commercial wood fibers from hardwood maple were used as

Table I   Formulations used in TiO_2-Pigmented Rigid PVC and Rigid PVC/Wood-Fiber Composites

Ingredients	Concentrations (phr)	
	Rigid PVC	Rigid PVC/ Wood-Fiber Composites
PVC (K value = 57)	100	100
Tin stabilizer (PlastiStab)	2	2
Calcium stearate (Synpro)	1.2	1.2
Paraffin wax (Gulf Wax)	1	1
Processing aid (Paraloid K-120)	1.2	1.2
Processing aid (Paraloid K-175)	1	1
Wood fibers	0	30
Aminosilane	0	1.5
Pigment (TiO_2)	0 and 10	0 and 10

fillers. These fibers were low-specific gravity (0.54), standard grade (20-mesh size or 850 μm) supplied by American Wood Fibers. γ-Aminopropyltriethoxysilane (Silquest A-1100 Silane, supplied by OSi Specialties–Witco) was used as a coupling agent to improve adhesion between wood fibers and the PVC matrix.[5,6] All materials were used as received from the manufacturers.

Compounding and Manufacture of the Composites

The dry blending of PVC, wood fibers, and other additives was carried out in a 20-L high-intensity mixer (Papenmeier, Type TGAHK20) rotating at 20.3 hp for 5 min. Two different formulations were used in this study: (1) the unpigmented formulations contained only PVC, 30 phr (parts per 100 resin) wood fibers, and 2 phr tin stabilizer, and (2) the TiO_2-pigmented formulations that contained a vast array of additives to ease the processability of the mixtures during compounding.[4,6] The addition levels of wood fibers and titanium dioxide in the pigmented mixtures were 30 phr and 10 phr, respectively. The concentrations of other additives were kept constant. Table I summarizes the pigmented blend compositions used in this investigation. For comparison, neat rigid PVC samples processed under the same conditions as rigid PVC/wood-fiber composites were also produced.

Once mixed, the dry-blended compounds were fed into the extruder's barrel through the hopper

for processing. A 19.1-mm single-screw extruder (Brabender, L/D ratio 30:1) driven by a 5-hp DC motor was used to process the blended compounds. A single-stage mixing screw (3:1 compression ratio) with a torpedo screw tip (35 degrees) was used during processing. The temperature profile from hopper to horizontal rod die was 165/175/185/185°C, and the rotational speed of the screw was set at 50 rpm.

The rod extrudates were compression-molded into panels (1.5 mm thick) to produce the specimens for UV weathering tests. Compression molding of the specimens was performed in a hydraulic, preheated press at 185°C and 4.5 MPa (650 psi) for 5 min. The mold was then cooled to room temperature, under pressure, by circulating cold water in the press. Samples of 150 mm × 150 mm were cut from the panel sheets for weathering tests.

Accelerated UV Weathering Tests

Accelerated artificial UV weathering tests were conducted in a QUV weatherometer that reproduces the damage caused by sunlight, rain, and dew. The samples were subjected to an accelerated weathering procedure by exposure to 340-nm fluorescent UV lamps (UV-B region) in the QUV Accelerated Weathering Tester. The weathering schedule involved continuous light irradiation and water spray for 18 min every 2 h. The average irradiance was about 0.85 W/m^2 at 340-nm wavelength with a chamber temperature of approximately 45°C. The sample condition was accessed every 200 h, for a total of 1200 h of accelerated weathering. Each assessment consisted of a visual examination of surface roughness or erosion, a contact angle measurement, a DRIFT-FTIR collection, and a color measurement.

Color Measurements

The surface color of unweathered and weathered samples was determined according to the procedure outlined in ASTM D2244.[22] A Microflash Elrepho model 200 Reflectometer from Data Color was used to measure color in $L^*a^*b^*$ coordinates at three locations on each sample. The L^* axis represents lightness; a^* and b^* are the chromaticity coordinates. In the CIELAB coordinates, $+a^*$ is for red, $-a^*$ for green, $+b^*$ for yellow, $-b^*$ for blue, and L^* varies from 100 (white) to zero (black). L^*, a^*, and b^* color coordinates of each sample, before and after exposure to QUV testing, were calculated on the basis of a D65 light source as established by the CIE 1976.[23] Color change (ΔE) was calculated using the following equation:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (1)$$

where ΔL^*, Δa, and Δb^* are the difference of initial and final values of L^*, a^*, and b^*.

Contact Angle and FTIR Spectroscopy Measurements

Contact angles of unweathered and weathered samples were measured with a Ramé-Hart Goniometer, model 100-00-115, equipped with an automated camera and image analysis software. Distilled water was used as the wetting liquid.

The infrared (IR) spectra of unaged and irradiated samples were obtained on a Mattson FTIR spectrophotometer (model Genesis II) at a resolution of 4 cm^{-1}. A total of 100 scans were coadded for each spectrum. IR absorbance spectra were measured over the range of 4000–500 cm^{-1} and diffuse reflectance FTIR was used for transfer of IR radiation.
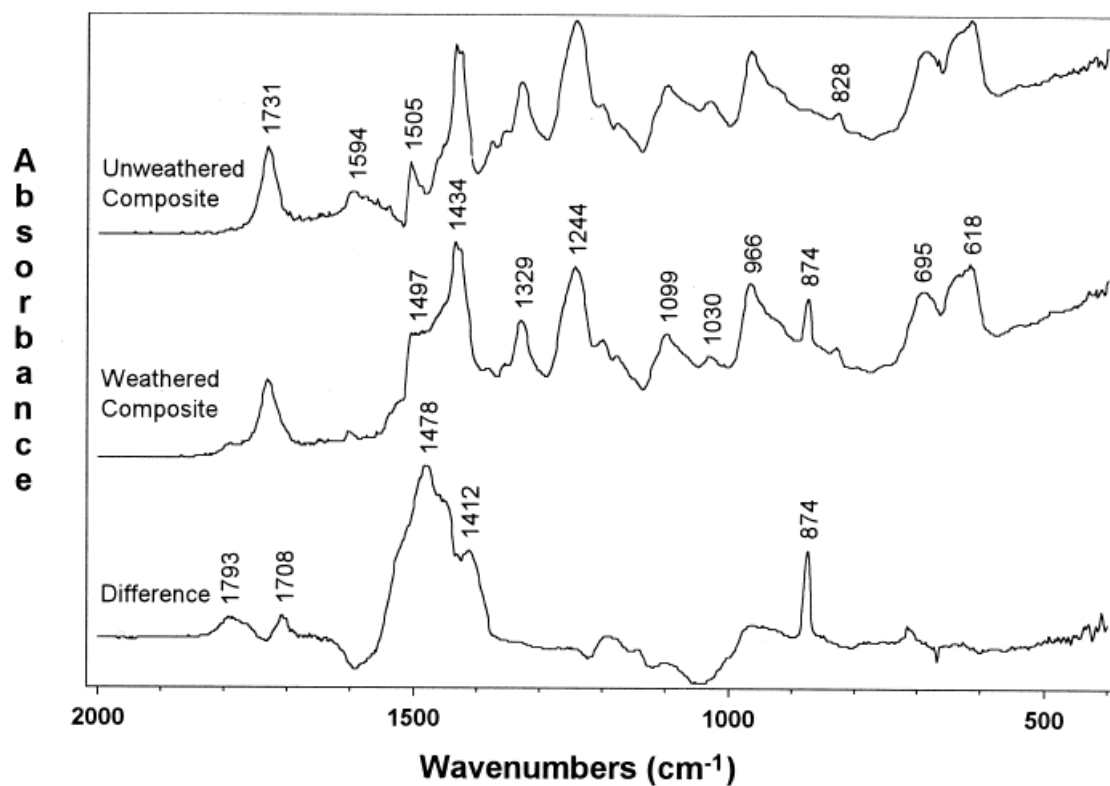
RESULTS AND DISCUSSION

Weathering of Unpigmented Rigid PVC/Wood-Fiber Composites

The FTIR spectra of neat, rigid PVC and rigid PVC/wood-fiber composites are illustrated in Figure 1(a) and (b), respectively; the spectra of both unweathered and UV-weathered samples are also shown. It can be seen that new absorption bands have emerged in the region of 1409–1478 cm^{-1} and at ~875 cm^{-1} after exposure to UV irradiation. The appearance of these new absorption bands is clearly seen in the difference spectra (weathered–unweathered) where groups frequencies associated with the formation of alkene or polyene linkages[24–26] are easily recognized at 1409–1478 cm^{-1} and 875 cm^{-1} (C=C stretching mode). The appearance of polyene units on the surface of the samples is indicative of photodegradation of the samples upon exposure to UV light.

The observed surface photodegradation process of unpigmented samples was also followed by measurements of the contact angles of a drop of water on the surface of unaged and UV-irradiated samples (Table II). Weathered samples exhibited
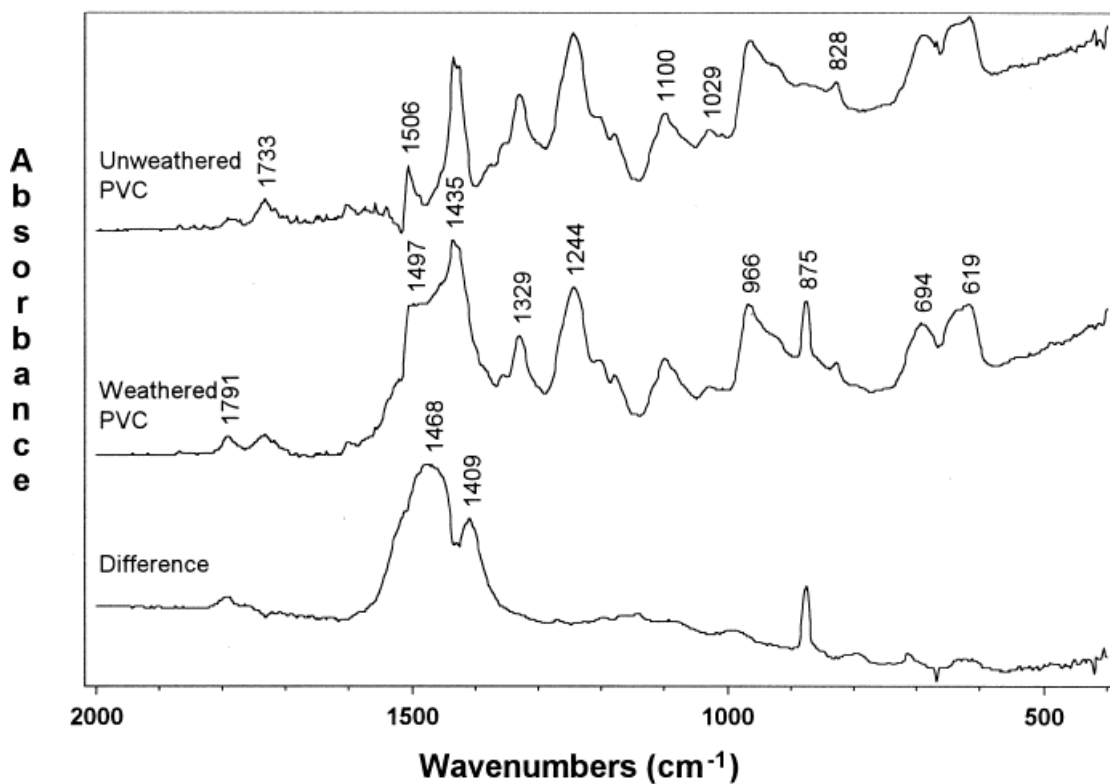
Figure 1 FTIR spectra of unpigmented (a) neat rigid PVC and (b) rigid PVC/wood-fiber composites in the region 2000–500 cm^{-1}. Both the unweathered and UV-weathered spectra, as well as the digital difference spectrum (weathered–unweathered), are illustrated.

Table II   Color Changes (Discoloration) and Contact Angles of Neat Rigid PVC and Rigid PVC/Wood-Fiber Composites Measured Before and After Accelerated UV-Weathering Tests
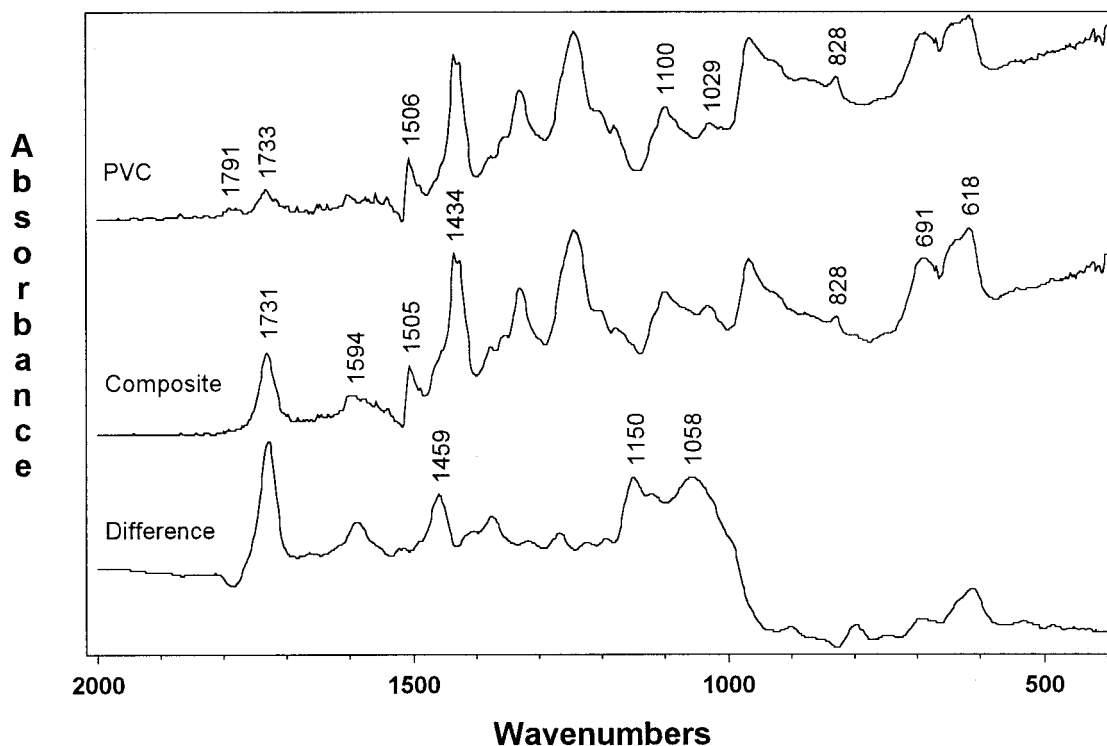
Samples	Color Change, ΔE	Contact Angle (°)	
		Before Aging	After Aging
Unpigmented			
Pure PVC	8.45	64	32
Composite	16.57	78	49
Pigmented			
Pure PVC + TiO_2	1.57	72	55
Composite + TiO_2	4.34	64	54

ing evidence [1409–1478 cm^{-1} and 875 cm^{-1} absorption bands in the difference spectra in Fig. 1(a,b)].

Measurement of color change (discoloration) provided additional evidence of photodegradation of the composites. The data in Table II indicate that the surfaces of both unpigmented neat rigid PVC and rigid composite samples exposed to UV light were severely modified and underwent color changes. This discoloration deeply affected the appearance of the degraded composites (the surface of weathered samples was covered with a thin layer of a white exudate). It should be noted that the composite samples exhibited greater discoloration than did neat PVC, suggesting that the incorporation of wood fibers into PVC matrix has a deleterious effect on the ability of the matrix to resist exposure to UV radiation.

The greater discoloration exhibited by the composite may be attributed to the incorporation of carbonyl functional groups from wood fibers within the polymer matrix during compounding. As shown in Figure 2, there are many differences between the spectra of unweathered neat, rigid PVC, and wood fiber-filled rigid PVC matrix. A

lower contact angle values (increased wettability) than the unweathered ones regardless of the addition of wood fibers. The increased wettability of the artificially weathered samples implied changes in their surface chemical compositions. The appearance of alkene linkages in the FTIR spectra of weathered samples provides support-

Figure 2   FTIR spectra of unweathered neat rigid PVC and rigid PVC/wood-fiber composite samples in the region 2000–500 cm^{-1}. The samples were not pigmented; the digital difference spectrum (composite-neat PVC) is also illustrated.

typical FTIR spectrum of unweathered neat rigid PVC showed two characteristic bands: a very broad one at 691 cm^{-1}, probably due to C—Cl stretching, and a sharp band at 1434 cm^{-1} due to C—H groups.[24,25,27,28] Some oxygenated structures were also detected in the PVC chain, as evidenced by the absorption around 1733 cm^{-1} and 1791 cm^{-1}, which can be attributed to carbonyl (C═O) groups. By contrast, the spectrum of the unweathered composite sample showed a dramatic increase in the absorption band intensity at 1731 cm^{-1}. A new band was also observed at 1594 cm^{-1}. These bands are characteristic of the main components of wood, and are clearly seen in the difference spectrum (composite - neat PVC) illustrated in Figure 2. The presence of cellulose is obvious from the very intense and sharp band appearing at 1731 cm^{-1}. This is due to the stretching vibration of carbonyl groups (C═O).[29] The two absorption bands at 1594 cm^{-1} and 1459 cm^{-1} are indicative of the presence of lignin, an aromatic compound, and are attributed to the C═C vibrations of the benzene ring.[30] The absorption bands at 1150 cm^{-1} and 1058 cm^{-1} are assigned to the ether linkages (C—O—C) from lignin or hemicelluloses.

Because wood contains oxidized compounds such as carbonyl groups, the increase in the relative intensity of the C═O stretching bands at 1731 cm^{-1} (Fig. 2) provided good evidence of the incorporation of carbonyl groups into the PVC matrix during blending. It is obvious from Figure 2 that the concentration of carbonyl groups has significantly increased after incorporating wood fibers into the PVC matrix. The presence of these carbonyl groups, that effectively absorb the incident light and initiate the dehydrochlorination reaction,[8] may explain the pronounced degradation observed in the composites as compared with the neat PVC. Although the addition of wood fibers into the PVC matrix was found to substantially accelerate the photodegradation of the PVC matrix, the FTIR results [Fig. 1(a,b)] suggest that the mechanism of photodegradation of the composite may be similar to that of neat PVC. The presence of alkene or polyene linkages is considered responsible for the photodegradation of both neat rigid PVC and rigid PVC/wood-fiber composites. When the sample is exposed to UV light, discoloration occurs rapidly due to the formation of alkene linkages and the resulting dehydrochlorination of the allylic chlorides in the polymeric matrix. This behavior may be represented as follows[8,9]:

$$[\text{—CH}_2\text{—CHCl—}]_n \xrightarrow{h\nu} [\text{—CH═CH—}]_n$$

$$+ \text{HCl} \quad \text{(dehydrochlorination)} \quad (2)$$
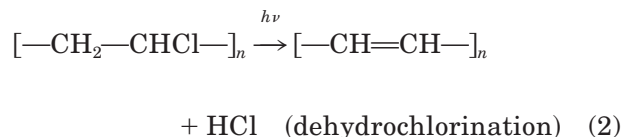
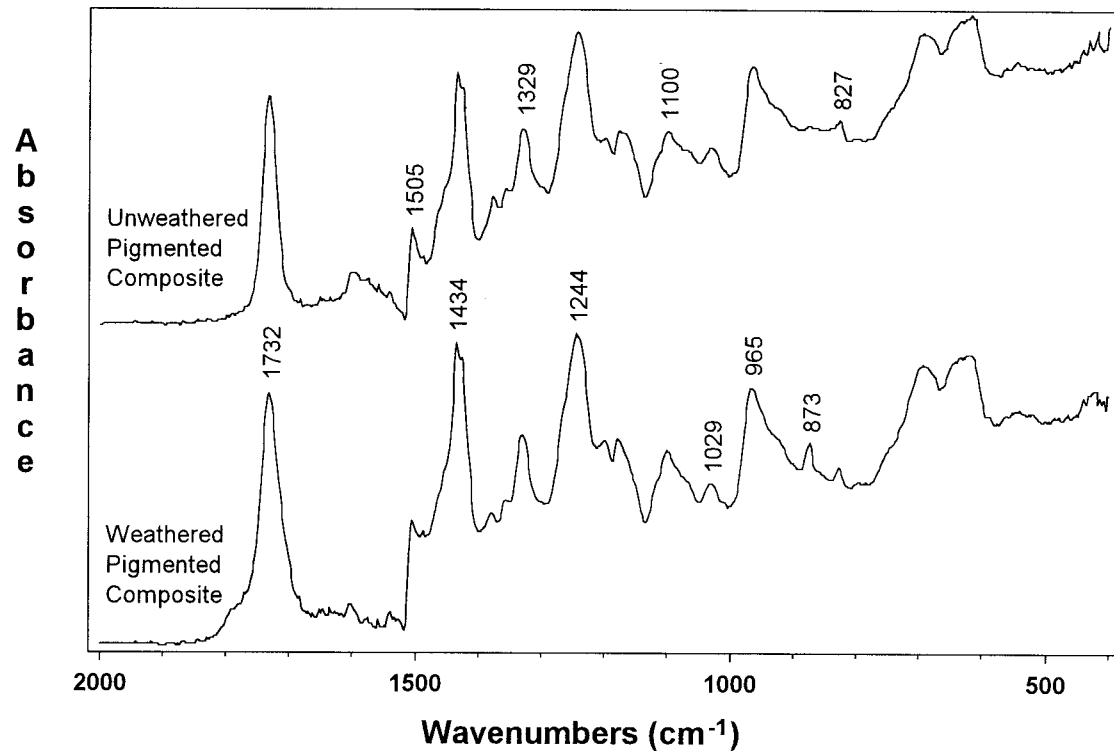## Weathering of TiO$_2$-Pigmented Rigid PVC/Wood-Fiber Composites

It has been reported that any system that prevents or delays the formation of chromophoric functional groups and polyenes during processing should provide a material with enhanced outdoor performance.[8–12,18] The usual practice is effectively to protect PVC products against light degradation by using adequate photostabilizer additives during processing.[11,12,18]

An attempt was made to enhance the ability of rigid PVC/wood-fiber composites to resist UV irradiation by incorporating 10 phr of rutile TiO$_2$ as a photoactive stabilizer during the composite's manufacturing. The data presented in Table II clearly show that the light stability of the composites can be improved quite efficiently with rutile TiO$_2$ stabilizers. This photoactive pigment afforded some protection to the samples against photodegradation by retarding the formation of polyene linkages, as revealed by the FTIR spectra of weathered neat rigid PVC and rigid PVC/wood-fiber composites [Fig. 3(a,b)]. The absorption band at ~875 cm^{-1}, which is typical of the polyene linkages,[24–26] showed a significant decrease in the concentration (area under the peak), as compared with unpigmented samples [Fig. 1(a,b)]. This observation implied that rutile TiO$_2$ inhibited the photodegradation process to some extent and was consistent with the discoloration results listed in Table II. The pigmented samples showed lower values of color change (ΔE) than the unpigmented ones. This significant decrease in the discoloration of pigmented samples treatments showed that the rutile TiO$_2$ provided stabilization during weathering of the samples.

It should also be mentioned that carbonyl groups were detected in the FTIR spectra of both neat rigid PVC and composites [Fig. 3(a,b)]. Since different formulations were used to manufacture the unpigmented and rutile TiO$_2$-pigmented samples, the presence of carbonyl functional groups in pigmented samples may be due to the additives (e.g., calcium stearate) used in the formulations of TiO$_2$-pigmented samples (Table I).
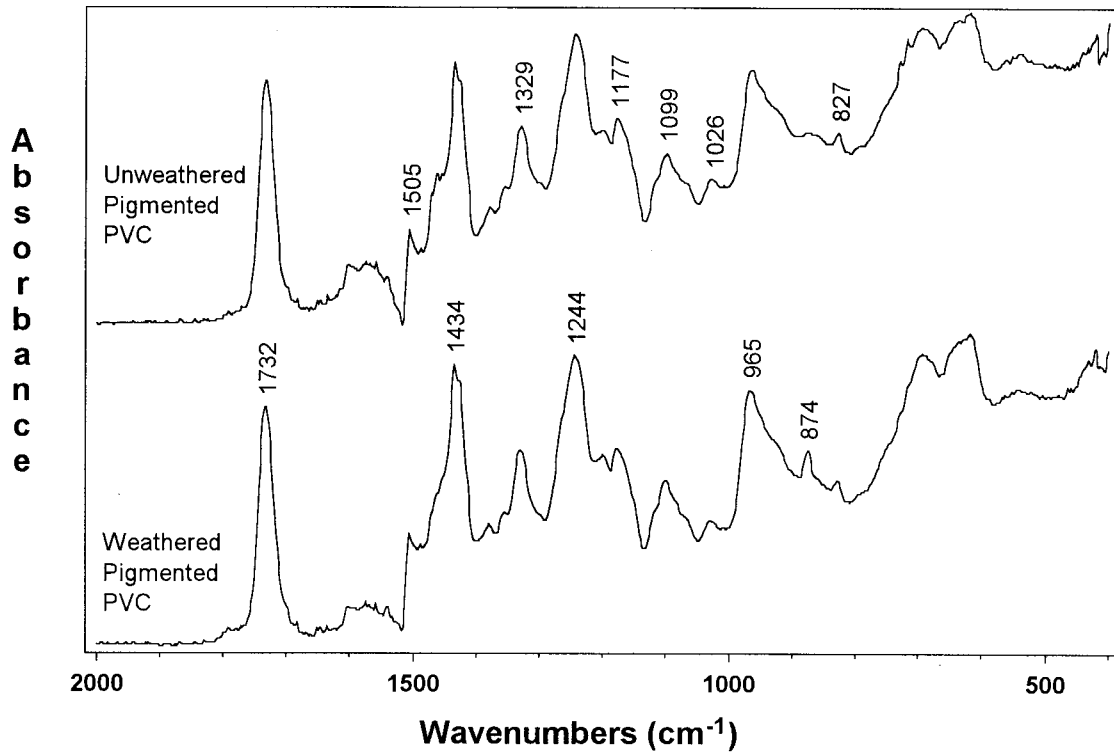
(a)

(b)

Figure 3 FTIR spectra of TiO_2-pigmented (a) rigid PVC and (b) rigid PVC/wood-fiber composites in the region 2000–500 cm^{-1}. Both the spectra of unweathered and UV-weathered samples are illustrated.

CONCLUSIONS

This study investigated the UV weathering performance of unpigmented and rutile titanium dioxide pigmented rigid polyvinyl chloride (PVC)/wood-fiber composites. From this investigation, it can be concluded that wood fibers are effective sensitizers and their incorporation into a PVC matrix accelerates the photodegradation of the PVC matrix when exposed to UV irradiation. Rigid PVC/wood-fiber composites can be produced that will provide quite satisfactory outdoor life. In formulating, one should attempt effectively to protect the PVC matrix against light degradation by using adequate photostabilizer additives (e.g., UV absorbers, photoactive pigments) during processing. Rutile titanium dioxide has proved very effective in providing stabilization during UV weathering of rigid PVC/wood-fiber composites by retarding the formation of polyene linkages during light exposure.

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