

Radiation Induced Degradation of WPC in the Field and in Laboratory Conditions

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Abstract

FTIR techniques were used to analyse the oxidation of polyethylene in WPC exposed to both accelerated and exterior weathering. UV-induced oxidation was found to be a surface and shallow subsurface phenomenon. The presence of wood in WPC was found to speed up the oxidation process, and different species of wood were found to have different effects. Additives may have unforeseen effects on oxidation; zinc borate was tested as an example of such an additive and found to slow the oxidation process. The ratio of various oxidation by-products was found to be similar for accelerated and exterior weathering samples, suggesting a similar mechanism of oxidation. Heat-induced stress cracking of WPC was also investigated. This phenomenon may be associated with composite degradation and failure, particularly in hot climates. The mechanism of such degradation appeared different from that of UV degradation in preliminary studies.

Electromagnetic radiation, mainly from the sun, interacts with all matter on the earth, including WPC. The focus of this presentation will be on two types of electromagnetic radiation: the short-wavelength ultraviolet radiation, and longer wavelength radiation in the range of infrared which is responsible for surface heating (see Fig 1).

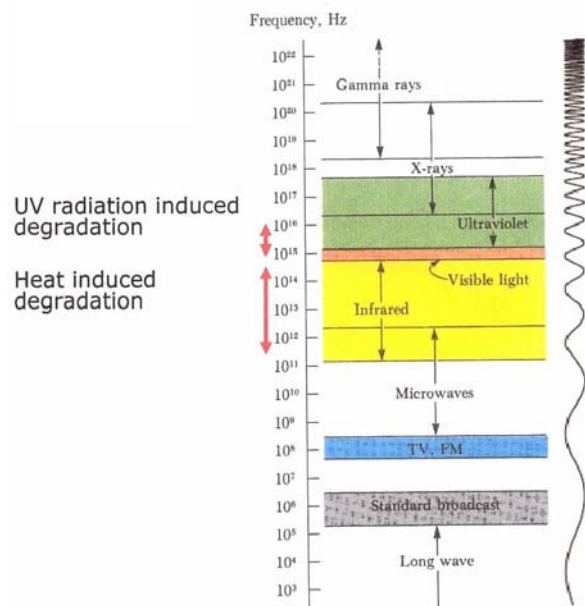


Figure 1. Electromagnetic radiation ranges

With respect to UV radiation, it is known that it can cause severe damage to the surfaces of many materials. In the case of wood plastic composites, UV radiation will generate colour fading (Fig 2), severe surface micro-cracking (Fig 3), accelerated wear (Fig 4), and increased microbiological activity in the form of fungal growth, including decay fungi and mould related discolouration (Fig 5). Microbiological activity is promoted by exposure of wood particles, as well as an increase in available food due to the breakdown of polymers and other organic compounds.



Figure 2. Colour fading due to ultraviolet radiation



Figure 3. Surface cracking and micro-cracking due to exposure to ultraviolet radiation



Figure 4. Wear acceleration by ultraviolet radiation



Figure 5. Acceleration of microbiological activity due to ultraviolet radiation

It is easy to see the results, but numerically measuring the WPC degradation caused by UV radiation is more difficult. Attempts have been made to link this degradation to mechanical properties¹, colour change of the surface², or measurement of changes in the chemistry of the material³. These changes can be conveniently detected and measured by a variety of instrumental methods, including infrared spectroscopy (FTIR)⁴.

In our work on WPC degradation by radiation, we focused on FTIR spectroscopy and the chemistry of polyethylene (PE) affected by UV radiation, with particular attention to polymer oxidation. There are three convenient ways to acquire infrared spectra of WPC and its polyethylene binder:

1. By collecting spectra from the sample surface using Attenuated Total Reflectance (ATR) methods. The analyzed surface can be relatively large, but must be smooth to allow good contact with the instrument (see Fig 6)^{3, 5}.



Figure 6. Infrared spectroscopic techniques - ATR

2. By collecting spectrum in ATR mode from a small segment of the surface using a special semi-micro ATR attachment (Split Pea). This allows the selection of an area for testing that is relatively free of wood, and the surface does not require a good finish (see Fig 7).

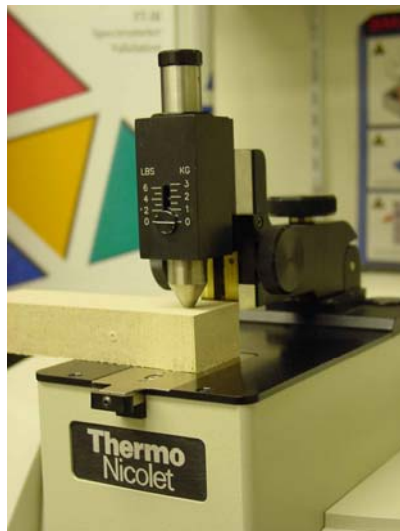


Figure 7. Infrared spectroscopic techniques – Semimicro ATR

3. By transmission of IR light through thin specimens cut from the WPC surface or pressed from the polymer recovered from the composite (see Fig 8). Recovery can be done by precipitation of PE from the solution after dissolving the WPC and filtering out all of the insoluble components, including wood. This last method allows high quality IR spectra to be obtained and information to be supplied that would not be available otherwise.



Figure 8. Infrared spectroscopic techniques - Transmission

In our work we used two methods: semi-micro ATR and transmission of polyethylene recovered from WPC. For the semi-micro ATR method, at least 27 spectra were collected and averaged for each measurement, and statistical analysis was performed on the results. Wood interference was kept as low as possible for each spectrum by minimizing the intensity of the intense wood cellulose ether band at 1100 cm^{-1} . For the transmission method, the polyethylene component of WPC was dissolved, and the wood and other insolubles were removed from the polyethylene solution using a $1\mu\text{m}$ to $2\mu\text{m}$ filter. The polymer was then precipitated, dried and pressed into film according to ASTM D 6645 using a 50μ shim.

Infrared spectroscopy of polyethylene, including the evaluation of UV photodegradation, is well known. Fig 9 shows the FTIR spectra of unexposed polyethylene and polyethylene exposed to

UV radiation. During exposure to UV in the presence of oxygen, polyethylene undergoes photo-oxidation and a number of compounds that contain carbonyl groups are created. The relative concentration of these products can be measured by the intensity of the absorption band around 1700 cm^{-1} (thin line) which can be quite strong and is not present in the unexposed sample (thick line). There is also a change in the amount of unsaturation visible in the intensity of the absorption band at 907 cm^{-1} , but this will not be further discussed in this paper.

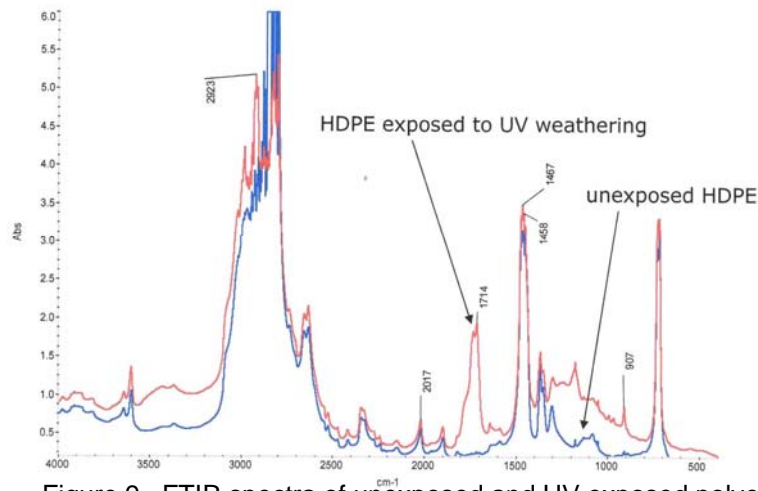


Figure 9. FTIR spectra of unexposed and UV exposed polyethylene

As was mentioned earlier, PE oxidation can be measured by the height of the carbonyl peak around 1720 cm^{-1} wavenumbers. A consistent number unrelated to the intensity of individual spectra may be expressed by the ratio of the carbonyl peak height to the height of another peak in the spectrum with intensity unaffected by the weathering process (a reference peak). This ratio is called the carbonyl index (see Fig 10). In our work, depending on the method of spectrum acquisition, absorption bands at 2018 cm^{-1} or 1467 cm^{-1} were used as reference peaks. The 1467 cm^{-1} reference peak is used after intensity correction to 100% polyethylene crystallinity⁶.

The carbonyl index can be calculated for spectra collected after various lengths of weathering exposure and plotted against weathering time, as is shown on a graph illustrating the progress of weathering in Fig 10.

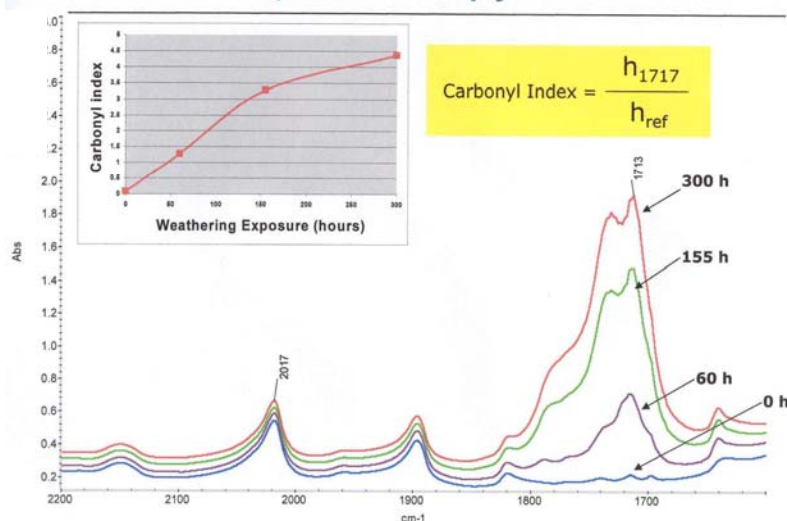
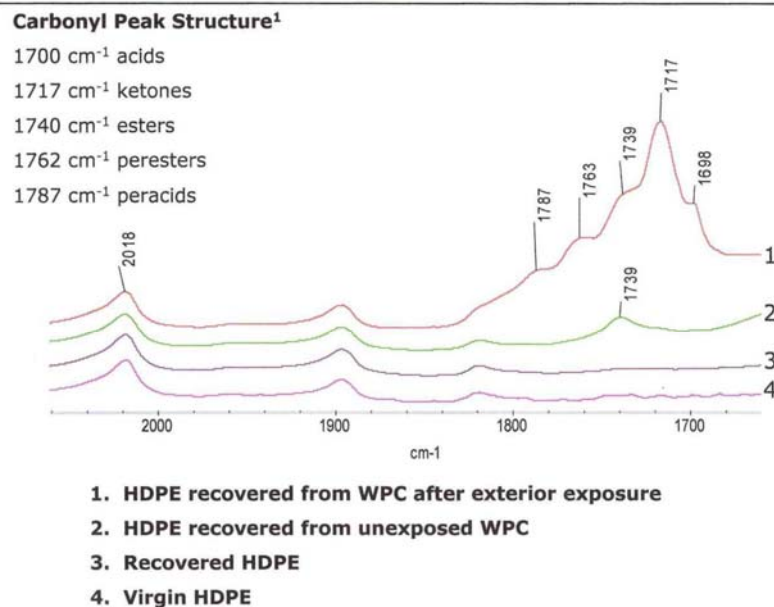


Figure 10. Carbonyl index measurement for oxidized polyethylene

Several polyethylene spectra are compared in Fig 11, including WPC. These spectra may be described as follows:

- Spectrum of virgin polyethylene – an almost flat line with no absorption bands in the region of interest.
- Spectrum of the same HDPE, dissolved and recovered as mentioned earlier – also showing no absorption bands in the carbonyl region.
- Spectrum of HDPE recovered from wood plastic composite. A weak carbonyl peak is shown, possibly due to oxidation during processing.
- Spectrum of HDPE recovered from WPC exposed to weathering. In this spectrum we can clearly see several individual absorption bands in the carbonyl region, which can be assigned as in polyethylene to specific compounds created during photo-oxidation⁷:
 - organic acids 1700 cm^{-1}
 - ketones/aldehydes 1717 cm^{-1}
 - esters 1735-1740 cm^{-1}
 - peresters 1762 cm^{-1}
 - peracids 1787 cm^{-1}



1. Luongo, J.P., *J Polymer Sci*, 1960. 42: p. 139-150.

Figure 11. Carbonyl peak structure of oxidized polyethylene

It is known that the intensity of these bands depends on the quantity of individual degradation products, and these depend on the chemical mechanism of oxidation.

Infrared spectra of polyethylene containing talc and lubricants, with and without 50% pine wood, are shown on Fig 12. Samples were exposed to 100 hours of accelerated weathering using fluorescent lamp radiation (QUV); unexposed reference samples are also shown. The carbonyl absorption band in WPC polyethylene became intense in comparison to weathered polyethylene alone, as well as unexposed WPC. The measured carbonyl index was 0.070 for weathered WPC, which is almost five times higher in comparison to the identically weathered polyethylene without wood (carbonyl index 0.015). This suggests that wood significantly accelerated the weathering of the polyethylene binder in these samples. This also demonstrates the difficulties that the industry faces in stabilization of WPC in comparison to polyethylene or polypropylene resins without wood.

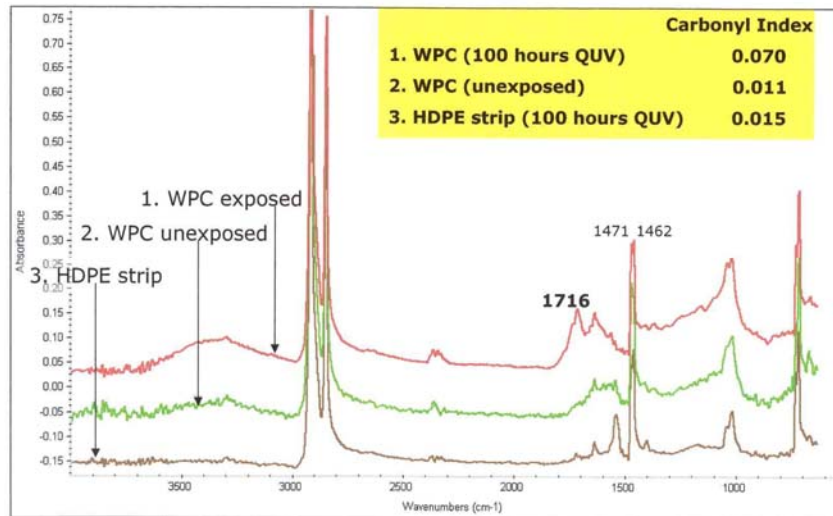


Figure 12. FTIR spectra of HDPE and WPC – unexposed and exposed to 100h QUV accelerated weathering

The comparison of carbonyl indices for two weathered WPC samples containing an identical quantity of 20 mesh pine and oak is shown in Fig 13. The presented data indicate that carbonyl indices are larger for samples made with pine than those made with oak. This means that, for the tested samples, pine accelerated the oxidation of polyethylene to a larger extent than oak

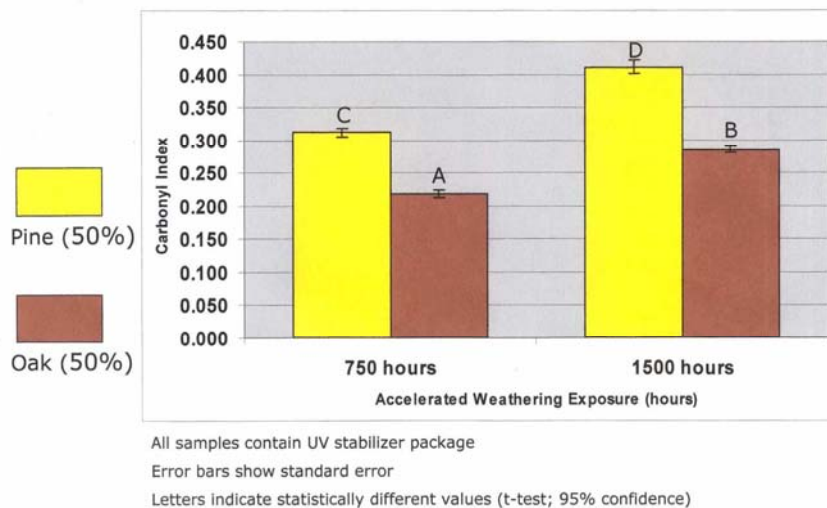


Figure 13. Comparison of carbonyl indexes of polyethylene in WPC containing different wood species

A series of carbonyl indices for WPC samples with and without UV stabiliser packages exposed to accelerated weathering (Fig 14) shows, as expected, a significant decrease in photo-oxidation for the sample containing the UV stabilizer package comprised of HALS and UV light absorbers (solid bars) in comparison to non-stabilized WPC (textured bars). Please note that the non-stabilized samples reached a carbonyl index plateau after only 500 hours of exposure, and a further slow decrease of the carbonyl index was observed, likely due to surface saturation and erosion. The carbonyl index slowly increased for the UV light stabilized samples and its intensity became equal to the carbonyl index of non-stabilized composites after 1250 hours of exposure.

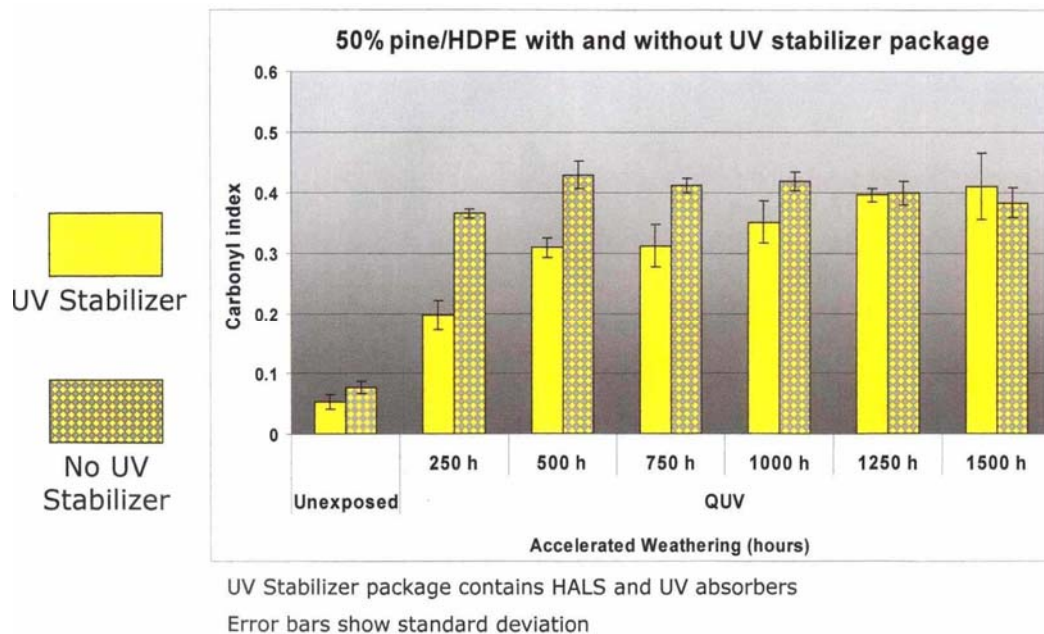


Figure 14. Changes of carbonyl indexes for WPC polyethylene with and without UV stabilizer during exposure to accelerated weathering

The effect of various additives on weathering of WPC could also be evaluated using the carbonyl index as shown on Fig 15. We use zinc borate, which is incorporated in some commercial products as a biocide, as an example. A decrease in the carbonyl index in samples containing zinc borate indicates that it seems to inhibit photo-oxidation in WPC containing HALS. Surprisingly, we also found that zinc borate inhibits photo-oxidation in WPC formulations without UV stabilizers, as can be seen in Fig 16. The mechanism behind this phenomenon is not fully understood, and requires further investigation.

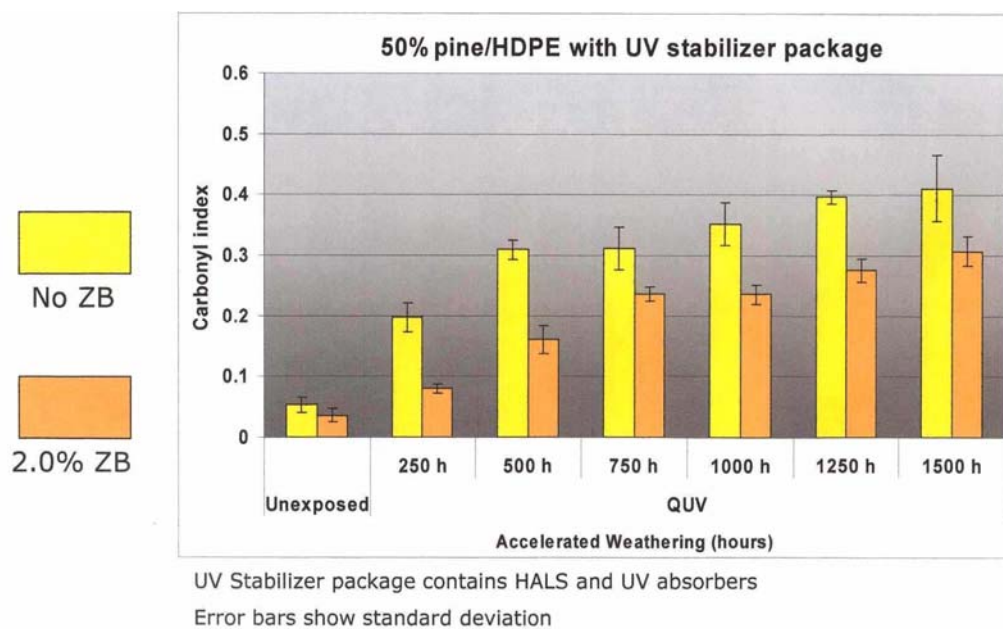


Figure 15. Changes in carbonyl indexes for WPC polyethylene with and without zinc borate

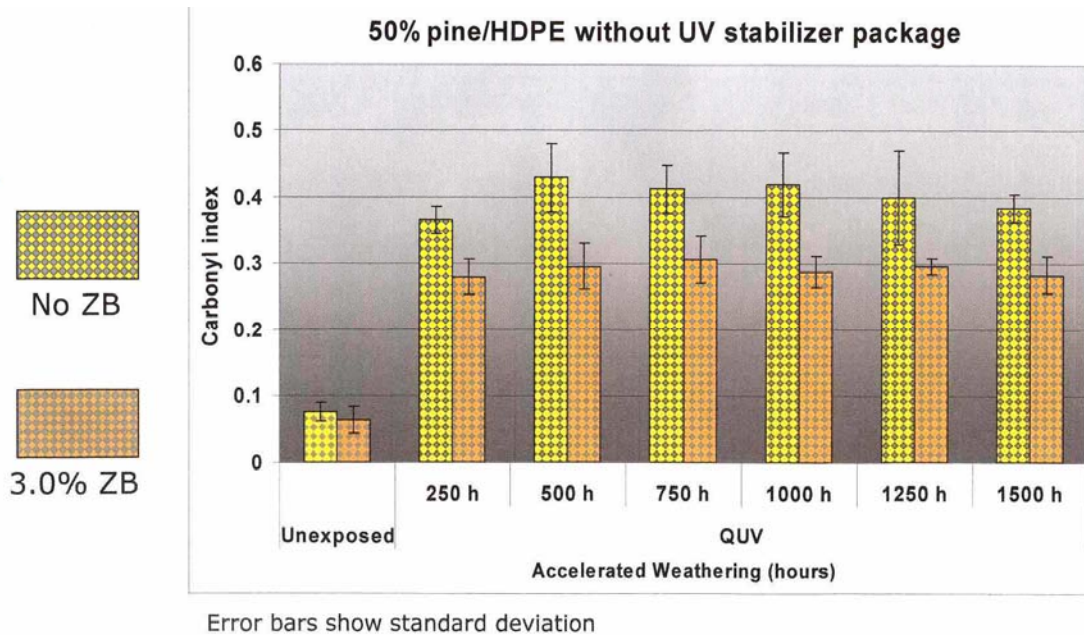


Figure 16. Changes in carbonyl indexes for WPC polyethylene with and without zinc borate

Further evaluation of the weathering of wood plastic composites, and the correlation between surface degradation and carbonyl index values is shown in Fig 17 and 18. Fig 17 shows the surfaces of samples discussed earlier, containing 50% wood, after 36 months exposure in Vancouver, British Columbia. Progressive damage and surface erosion is well visible and corresponds with the trend in carbonyl index values, particularly those measured after only 4 months of exposure. An identical trend can be seen for samples with similar polyethylene binder composition but wood content of 65% (see Fig 18).

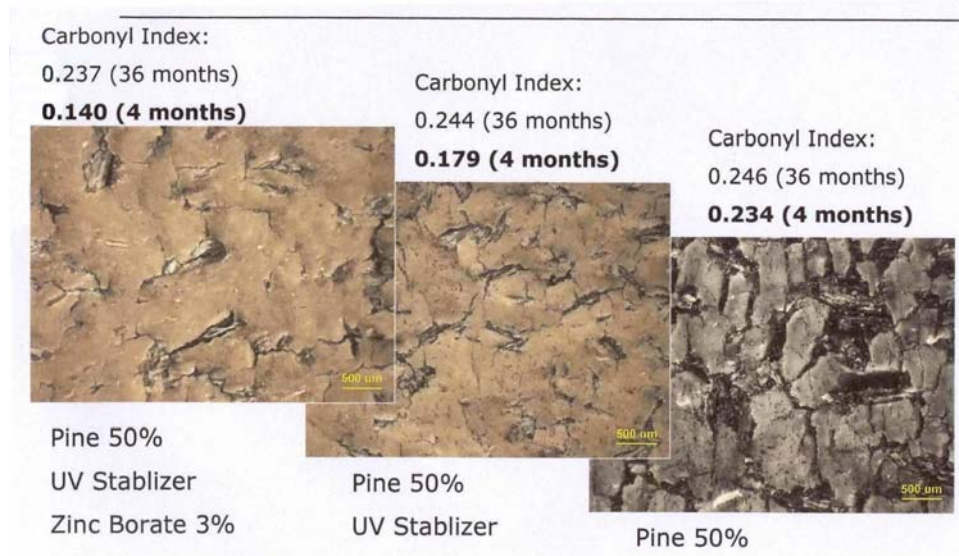


Figure 17. Appearance of samples of WPC vs. carbonyl index value after 36 months exterior exposure

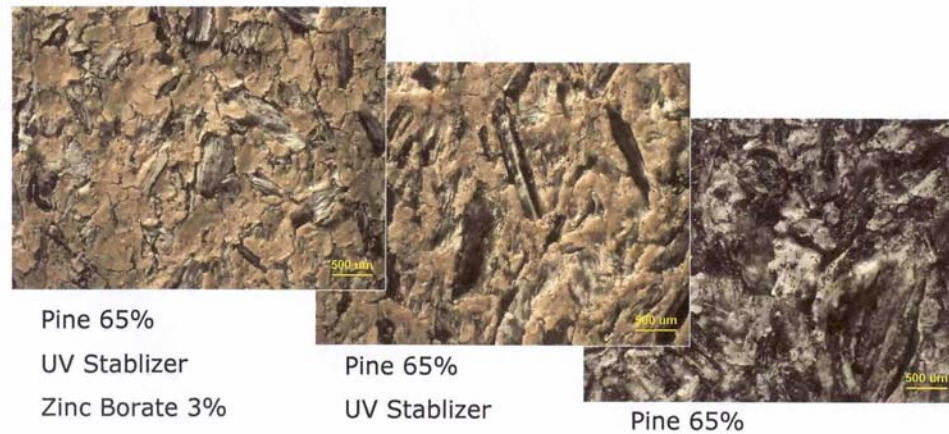


Figure 18. Appearance of samples of WPC after 36 months exterior exposure

As can be seen from the above data, the described test has the potential to become an early (just a few months) and effective indicator of the long term performance of wood-plastic composites exposed to weathering. Longer exposure (years) seems to lead to saturation of the carbonyl index value, particularly when it is calculated from spectra acquired using the convenient semi-micro ATR method. It also should be mentioned that many additives used in WPC manufacturing have the potential to become UV degradation inhibitors or accelerators due to surface activity or contaminants present, and should be tested in this respect prior to use.

What does 4 months of exterior exposure mean with respect to the duration of accelerated weathering (Fig 18)? Data presented in Fig 19 help to answer this question. A comparison of the carbonyl index for a sample containing 50% pine after exposure for 4 months in Vancouver to carbonyl indexes measured during accelerated weathering using a QUV instrument showed that approx. 400h artificial weathering is equivalent to 4 months of summer exposure in southern British Columbia, Canada. Similar comparisons showed that 4 months in a sunny California summer equals roughly 650h of accelerated weathering and 4 months in a cloudy Hawaiian winter was equal to only 200h despite the southern location. For longer exposure times, this correlation was not linear. For example, 36 months in Vancouver seemed to correlate to only 1000h of accelerated weathering. This non-linear correlation is likely due to heavy erosion and the effects of microbiological activity during exterior exposure. It also should be mentioned that this comparison applies only to photo-oxidation, which is important but is not the only process associated with weathering.

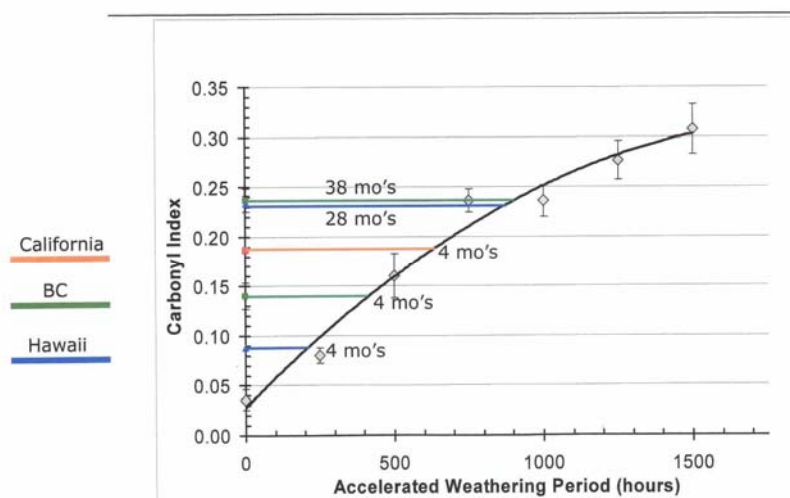


Figure 19. Correlation of accelerated weathering to exterior exposure

Detailed analysis of individual WPC absorption bands in the carbonyl region shows similar relative intensity of the various bands for both accelerated weathering and California exterior exposure samples (Fig 20). This indicates that the photo-oxidation mechanism is quite similar for radiation from the fluorescent lamp used and sunlight in sunny California.

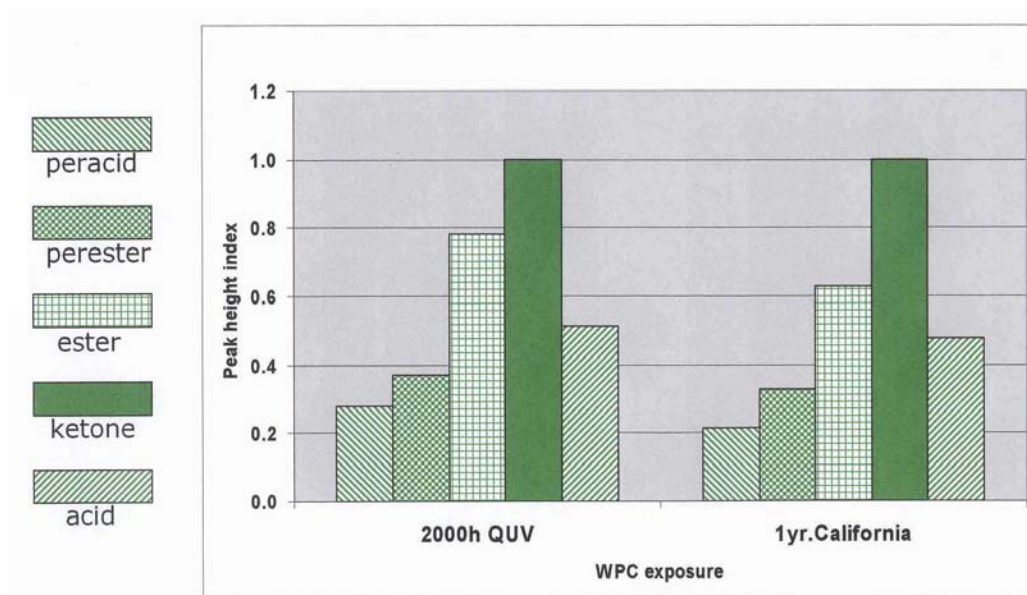


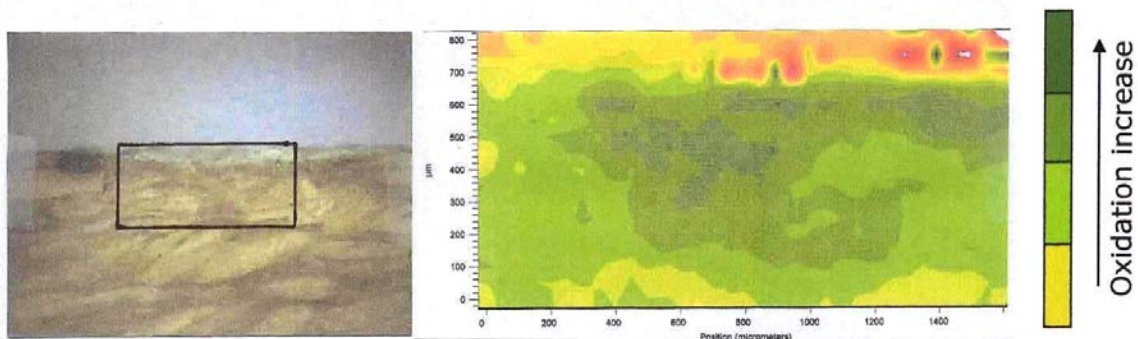
Figure 20. Carbonyl peak structure for HDPE recovered from WPC after 2000h QUV accelerated weathering and after exposure in California

The depth of the interaction of UV light with WPC made without light absorbers or stabilizers was also analyzed. When we looked at the exposed sample cross-section using an optical microscope, we could distinguish the white layer of degraded material with a thickness of 0.3 – 0.5 mm (Fig. 21). Raman microscopy of the same sample (Fig. 22) showed increased intensity of the carbonyl absorption peak indicating increased photo-oxidation up to 0.6 – 0.7mm in depth below the material surface. This indicated that UV induced degradation of WPC is most likely a surface and near surface phenomenon only.



Figure 21. Depth of UV degradation after 2000 hours QUV as seen under optical microscopy

Raman spectroscopy* oxidized HDPE layer thickness ~0.6 mm



* Courtesy Thermo Nicolet

Figure 22. Depth of UV degradation after 2000 hours QUV exposure as seen by Raman spectroscopy

When inspecting WPC materials exposed to exterior conditions, particularly in full sun locations in a hot climate, the development of deep cracks can be observed (Fig. 23). The depth of the cracks indicates that it is unlikely that UV radiation is the cause, and heat generated by infrared radiation is a likely culprit. The size of the cracks varies from small cracks visible during careful inspection to large cracks that lead in some cases to total disintegration of the WPC boards, as was described a year ago in Toronto⁸. The association of these cracks with stress is more or less obvious. The cracks seem to develop during the lifespan of all WPC in exterior exposure, months or even many years after installation, and frequently become the centre of biological activity where fungi fruiting bodies appear (Fig. 23). This type of failure progresses much faster and more aggressively in the same composite in a hot climate with full sun exposure than when exposed in shadow or a climate with a moderate temperature.

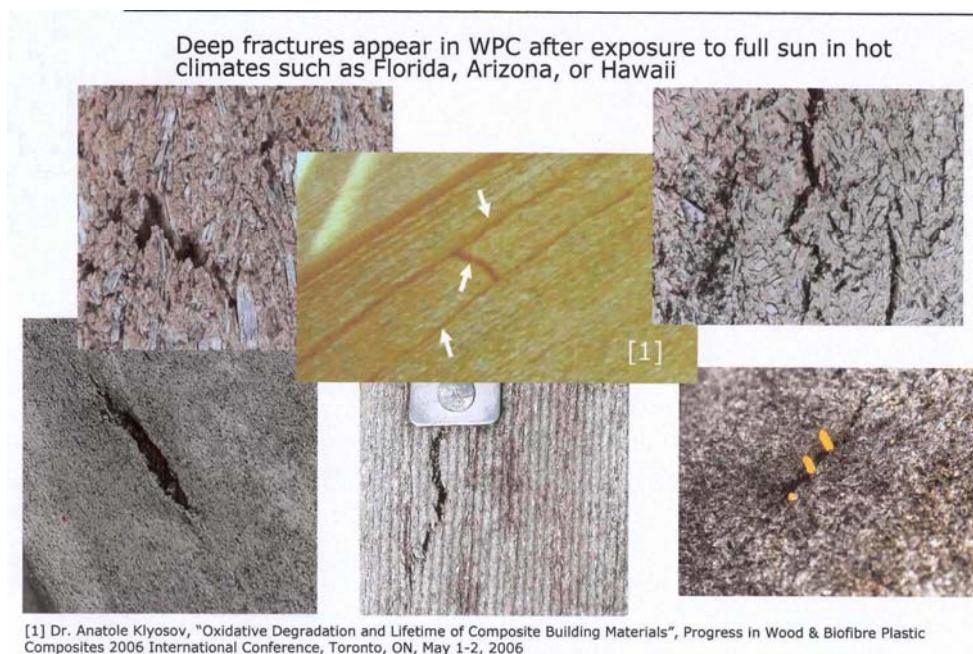


Figure 23. Stress cracking in WPC

We had the opportunity to evaluate in detail a sample of WPC exposed in Florida for over 10 years. The evaluation focused on a few square inches in the vicinity of a crack (Fig. 24). Wood content found in corresponding types of WPC (used here as a reference) was 50-55% vs. only 14% near the surface of the Florida sample and almost total wood depletion (3%) in the interior of the sample (Table 1). Scanning electron microscopy showed the exterior of the sample to be full of debris from the porous polyethylene binder and some wood remains. Visible fungal mycelia filaments indicated that decay fungi were likely responsible for the wood depletion (Fig. 25).

Table 1. Wood content of Florida sample

| Sample Description | Distance from Surface mm | Wood Content % |
|-------------------------|--------------------------|----------------|
| Reference | NA | 50 - 55 |
| Florida sample surface | 0 - 2 | 14 |
| Florida sample interior | 2 - 6 | 3 |



Figure 24. Evaluated sample of Florida WPC

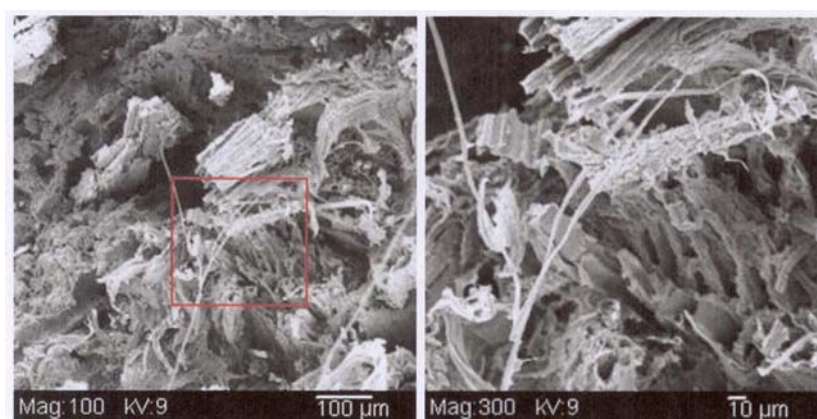


Figure 25 Scanning electron microscopy of Florida sample interior

TIR evaluations of the carbonyl absorption band for polyethylene recovered from the interior and surface of the sample are shown in Fig. 26. While strong oxidation of the sample surface seemed obviously due to UV exposure, it was quite surprising that oxidation of polyethylene recovered

from the sample interior 2-6mm below the surface was much stronger, with the carbonyl index almost three times higher for the interior. This oxidation cannot be easily explained.

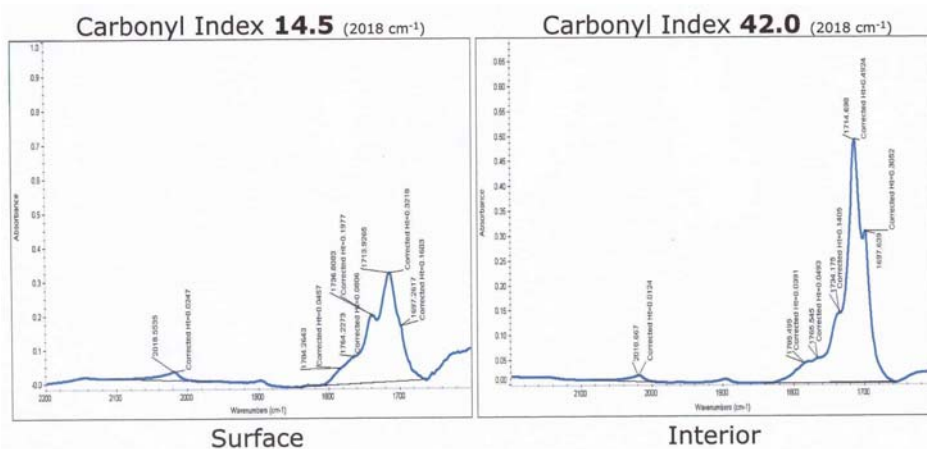


Figure 26. FTIR spectroscopy of polyethylene recovered from the surface and interior of the Florida sample

Comparison of the relative intensity of IR absorption bands in the carbonyl region for the Florida field sample and a WPC sample exposed in California lead to an interesting observation. The carbonyl peak structure for the surface of the samples exposed in Florida and California seemed to be very similar. On the other hand, the carbonyl peak of the polyethylene recovered from the interior of the Florida sample seemed to be significantly different (Fig. 27). This most likely indicates that the oxidation process of the surface and interior of the Florida sample were controlled by different factors.

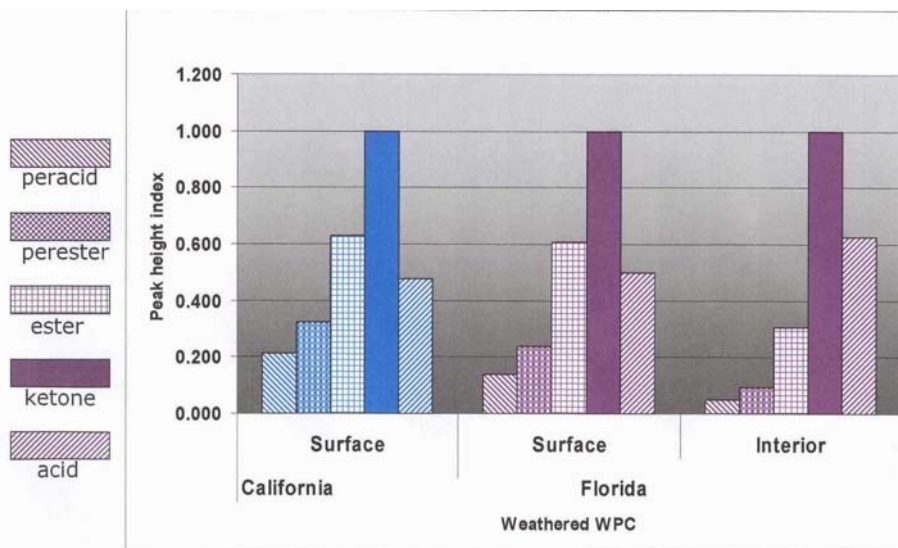


Figure 27. Analysis of the absorption band in the carbonyl region for polyethylene recovered from the Florida sample

Differential scanning calorimetry of polyethylene from the Florida sample also showed differences between the reference, surface, and interior samples (Table 2). An increase in heat of fusion from 100 J/g for the reference to over 140 J/g for the interior sample most likely indicated a significant decrease in the molecular weight of polyethylene and the cause of this process also cannot easily be identified.

Table 2. Differential Scanning Colorimetry for polyethylene recovered from Florida sample

| Sample Description | Heat of Fusion of Polyethylene °F |
|-------------------------|-----------------------------------|
| PE Reference | 100 |
| Florida sample surface | 100.8 |
| Florida sample interior | 142.0 |

CONCLUSIONS

- Various FTIR techniques can be used to track the oxidative degradation of polyethylene binder in WPC. Analysis of FTIR spectroscopic data can be used for assessment of the relative progress of weathering and the effect of different additives.
- Wood can accelerate photo-oxidation of polyethylene in WPC. The intensity of the process seems to be related to wood species.
- Some additives commonly used in WPC may have a positive or negative effect on polyethylene photo-oxidation. Zinc borate can be seen as an example of a biocidal additive which also inhibits photo-oxidation.
- Samples of polyethylene based WPC exposed to fluorescent lamp induced accelerated weathering or exterior conditions develop very similar patterns of oxidative degradation by-products. This indicates that the weathering process seems to be similar in both cases.
- WPC degradation by UV light seems to be only a surface and shallow subsurface phenomenon.
- FTIR analysis of WPC after a few months of exterior exposure may serve as an indicator of long-term performance.
- Heat induced stress cracking of WPC seems to be a weathering process capable of reaching further into the composite. Stress cracking in older materials may be associated with further composite degradation.
- The mechanism associated with WPC degradation in the field seems to be not fully understood. Further study is required, particularly related to subsurface degradation.

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