

EVALUATION OF WOOD PLASTIC COMPOSITE PHOTO-DEGRADATION USING MODERN MICROSCOPIC AND SPECTROSCOPIC METHODS

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INTRODUCTION

Wood-plastic composites (WPC) are a new generation of polymeric materials made from wood particles and thermoplastic resin. Polyolefins, particularly polyethylene, are used commercially as binders. Hardwoods or softwoods can be incorporated into the resin in quantities of 50 – 70%. However, compositions exceeding 80% of wood are known.

Significant interest in WPC was created recently in North America, particularly due to the voluntary withdrawal in December 2003 of CCA treated wood from residential construction by all major lumber suppliers. Extruded wood plastic composite decking and railing products seem to be rapidly filling this niche with the predicted North American production of almost one billion dollars in sales in 2005. It also has to be mentioned that manufacturers of WPC are major users of recycled polyethylene films including shopping bags.

It is known that the surface of WPC decking boards undergoes rapid photo-degradation. As a consequence of this degradation, microcracks appear on the surface which may lead to significant colour change and enhancement of microbiological activity (which appear initially on or near the surface). To protect wood composite from potential decay of the wood portion of the material, zinc borate (ZB) is frequently added as a biocide.

It was also found that Hindered Amine Light Stabilizers (HALS) are frequently not fully effective in WPC protection of

polyolefin polymer against photo-degradation. However, there is not a known publication that addresses accelerated photo-degradation in WPC materials.

In the presented work, model polyethylene based WPC was evaluated with and without zinc borate (ZB), selected HALS, and organic UV absorbers used in combination with inorganic pigments. For comparison purposes, similar systems without the wood and inorganic pigments extruded in the form of 50 μm thick film were also tested.

FTIR spectroscopy was selected as a primary method for assessment of photo-degradation with focus on the absorption band at 1718 cm^{-1} . Weathering of pure polyethylenes and methods of weathering process evaluation, including infrared spectroscopy are well known¹ but little work has been done on filled polyethylene materials, particularly where filler and other additives may be active during the photo-degradation process.

OBJECTIVE

The objective of the presented work was to identify the most suitable method for assessment of the photo-degradation process in WPC and quantitatively evaluate the degradation of the polyethylene binder with and without UV stabilizers.

¹ References

- [1] Carrasco, P.; Saurina, F.; Colom, J Appl. Polym Sci.,60, 153-9, 1996
- [2] Hamid, S.H.; Maadhah, A.G. Arabian J. Sci. Eng., 13, 503-31, 1988
- [3] Yang, C.Q.; Fateley, W.G. Anal. Chim. Acta, 194, 303-9, 1987
- [4] Weiner, L.R. '71 Soc. Aerosp. Mater. Process Conf: Eng., Nat Symp. Exhib 16th, 85-96, 1971

EXPERIMENTAL

1. SPECIMEN EXTRUSION

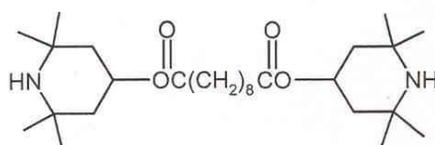
a) Wood Plastic Composites

A variety of WPC's (see table 1) were extruded using a Cincinatti Milicron E-55 extruder with 55 conical counter-rotating screws and Strandex die.

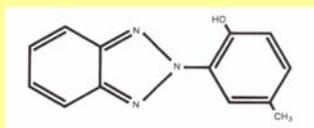
Table 1. Composition of Wood Plastic Composite Materials

Materials	1	4	5	6	8	11	27	28	31	33
1. HDPE Solvay B53-35H-001	36.97	36.37	45	44.29	24.06	23.66	36.58	36.97	23.79	24.06
2. Pine Wood (20 mesh)	49.79	47.54	51	48.71	65.93	63.42	-	-	-	-
3. Oak Wood (20 mesh)	-	-	-	-	-	-	48.28	49.79	64.26	65.93
4. UV Stabilizer package*	9.24	9.09	-	-	6.01	5.92	9.14	9.24	5.95	6.01
5. Zinc Borate	-	3.0	-	3.0	-	3.0	2.0	-	2.0	-
6. Lubricants	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
7. Talc	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

*UV Stabilizer package – Tinuvin 770 (Ciba) 5 pbw, Tinuvin P (Ciba) 5 pbw, metal oxides pigments-15%, HDPE (carrier) – 75%



Bis (2,2,6,6,-tetramethyl-4-piperdy) sebacate (HALS)
(Tinuvin 770)



2-(2H-Benzotiazole-2-yl)-4-methylphenyl
(Tinuvin P)



Zinc Borate (ZB)
(Borogard)



Extrusion of samples of WPC at Washington State University in Pullman, WA (USA)

b) Polyethylene Films

Reference samples of polyethylene films (see table 2) were extruded using a Brabender Plasticorder single screw extruder, equipped with 10 cm wide ribbon die and take off equipment.

Table 2. Composition of reference polyethylene films

PE ID	1F	6F	7F	8F	10F	11F	13F	14F	1F(H)
1. HDPE	-	-	-	-	-	-	-	-	100
2. LLDPE/LDPE	100	99	98	96	99	99.4	95.4	98.4	-
3. ZB%	-	1	2	4	-	-	4	-	-
4. ZnO%	-	-	-	-	1	-	-	1	-
5. Tinuvin 770	-	-	-	-	-	.3 %	.3%	.3%	-
6. Tinuvin P	-	-	-	-	-	.3%	.3%	.3%	-

2. WEATHERING EXPOSURE

a) Weathering of WPC

WPC samples were exposed to QUV (fluorescent lamp apparatus) accelerated weathering

Conditions a: 8h UVA 340 lamps @ 0.68W/m²/nm/ at 60°C, 5 min spray, 3.55h condensation at 50°C

b) Weathering of Polyethylene Films

Reference films were exposed to QUV accelerated weathering:

Conditions b: 8h/UVB 313 EL lamps @ 0.44W/m²/nm/@60°C and 4h condensation at 50°C

Conditions c: 6h/UVB 313 EL lamps @ 0.77W/m²/nm at 60°C/4h condensation at 50°C, 6h/UVB 313 EL lamps @ 0.77 W/m²/nm at 60°C and 8h sulphuric acid (pH2) spray and dry @ RT

3. EVALUATION

a) Optical and SEM microscopy

For optical microscopy, a Leica M212 stereoscopic microscope with 1.6 PLAN APO lens, Panasonic GP522H video camera and Sony UP-2100 printer were used. For SEM microscopy a 2002 Hitachi S-3000N variable pressure scanning SEM with automatic stage and Quartz Xone EDX were used.

b) Colour Change

Colour change evaluation was carried out using a Gretag Macbeth, Color Eye XTH (ASTM D2244)

Measurement conditions: colour equation LCH, angle 10 deg., illuminant D 65, reflectance mode with regular aperture.

c) FTIR ATR (Split Pea)

Surface photo-oxidation was evaluated using an Avatar 3700 FTIR spectrometer with a Split Pea ATR device (silica crystal). In quantitative evaluation absorption band at around 1718cm⁻¹ was used with 1470cm⁻¹ band as a reference.

d) FTIR Transmittance

FTIR transmittance using an Avatar 3700 spectrometer was carried out for 50 – 60 µm polyethylene films extruded or compression moulded from polyethylene recovered from weathered WPC. An absorption band at 1718cm⁻¹ was taken under consideration with 2018cm⁻¹ peak as a reference.

PE recovery: specimens 12 x 50mm with thickness of 0.5mm ±0.05mm were cut from the surface of weathered wood plastic composites. Specimen was placed in 200 mesh stainless steel cage and boiled in 100 ml xylenes (bp: 136° - 140°C) or ethylbenzene containing 1% antioxidant. After 8h, hot solvent with dissolved polyethylene was filtrated through glass fibre fillers (2.7 µm). To warm filtrate, 17g of n-heptane was added to promote polyethylene precipitation. Precipitated polyethylene was rinsed with (1) warm toluene, followed by (2) n-heptane and then dried.

e) Raman Microscopic Spectroscopy

FT-Raman spectroscopy of specimen's surface and cross-section using a Nicolet Nexus 370 equipped with a Raman Module accessory. Raman microscopic studies were performed using a ViewStage accessory for the FT-Raman module (Thermo Electron Corp).

f) pH of Wood Plastic Composites

pH was measured using a water solution obtained by boiling ground WPC (40 mesh) in distilled water for 30 minutes. An Orion model 230A pH meter was used for measurement of extract acidity.

g) UV Absorption

UV absorption of 53 µm films was measured using a Unicam UV4 spectrometer in the wavelength range of 270 nm to 600 nm.

COMMENTS AND CONCLUSIONS

1. The surface of wood plastic composites undergoes fast weathering which can be visible under microscope in the form of cracks exposing the wood. This is reflected in significant colour change, particularly as whitening. Weathering of WPC can be monitored by FTIR spectroscopy.
2. The WPC surface seems to weather faster in comparison to pure polyethylene which is visible in FTIR ATR spectra.
3. The most sensitive method for evaluation of weathering of WPC seems to be the measurement of IR transmittance at 1718 cm^{-1} for polyethylene recovered from the surface of the exposed samples.
4. It was identified, based on FTIR spectroscopy data, that zinc borate used historically in WPC for biocidal purposes also seems to retard the weathering of wood plastic composites.
5. Tested Hindered Amine Light Stabilizer is very sensitive to an acidic environment which significantly reduces its activity. It is also expected that many other HALS will perform similarly to the tested compound.
6. It was found that zinc borate increased the pH of WPC. This is likely one of the factors responsible for the decrease in weathering of WPC protected by HALS.

7. It is also expected that the acidity of the wood plastic composites may be increased by acid rain in the natural environment, and zinc borate as a WPC additive may be even more beneficial than laboratory experiments indicate.
8. Zinc borate likely influences the photo-chemistry of the wood, which is visible through different patterns of colour change of WPC during weathering. Wood itself is known for a strong sensitivity to weathering and many compounds present in wood likely act as photo-degradation initiators. There is a possibility that zinc borate neutralizes these compounds.
9. It was also found that zinc borate does not seem to retard weathering of pure polyethylene and does not contribute to a meaningful increase of UV absorption by polyethylene.
10. Surprisingly, it was also found that zinc oxide used in one of the experiments increased photo-oxidation of polyethylene (regardless of the acidity of environment) when resin was compounded with HALS and UV absorber.

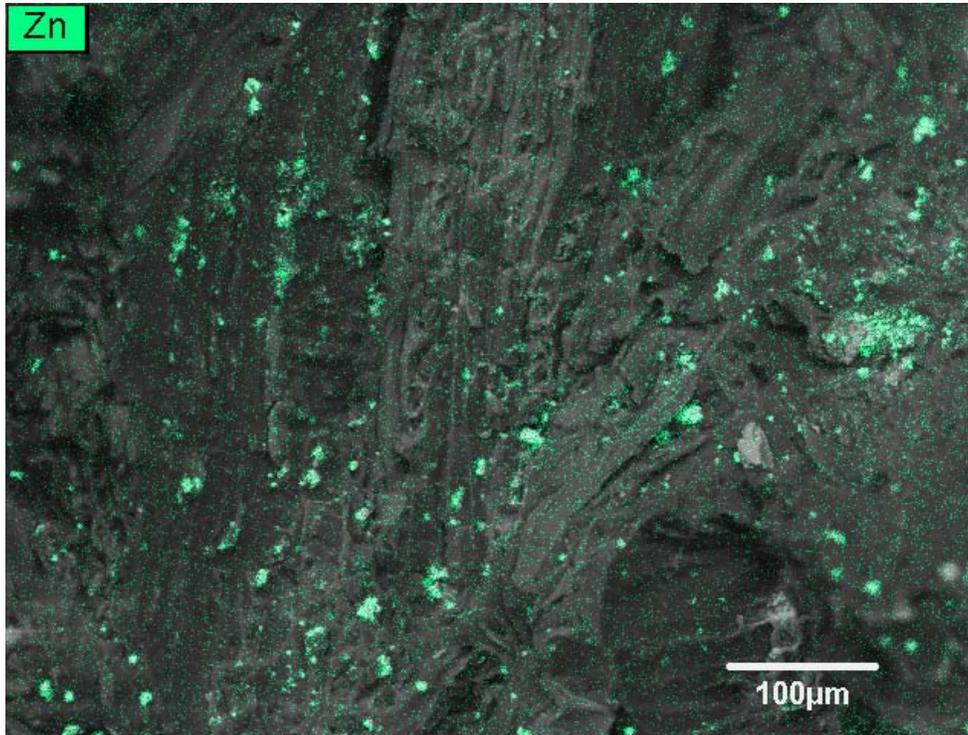
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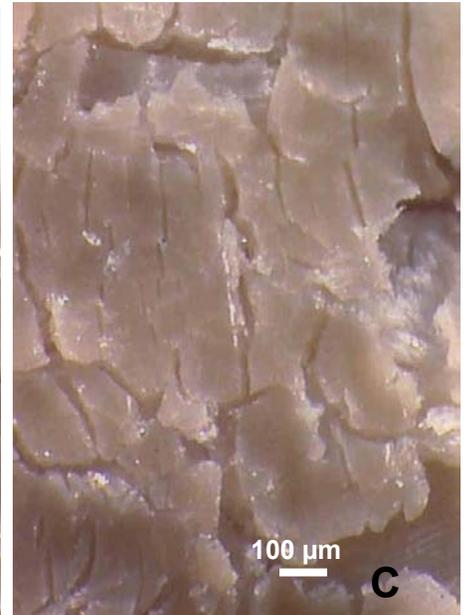
The presented data is the result of an initial evaluation and future results based on more extensive data collection may vary to some degree from those shown above.

RESULTS

MICROSCOPIC EVALUATION

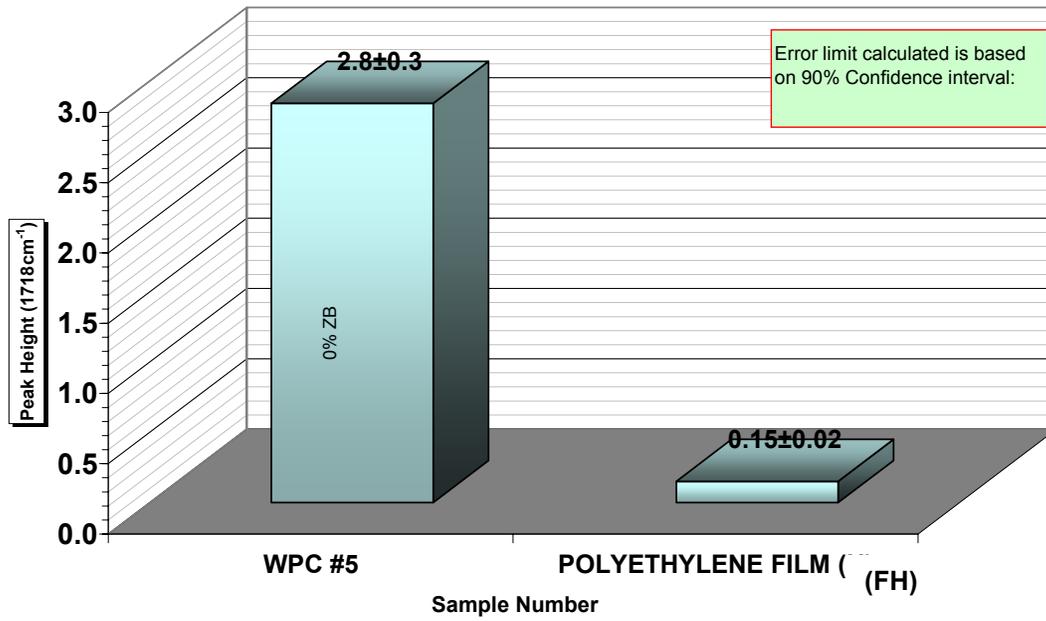


SEM picture of WPC fracture with mapping zinc borate (Green)

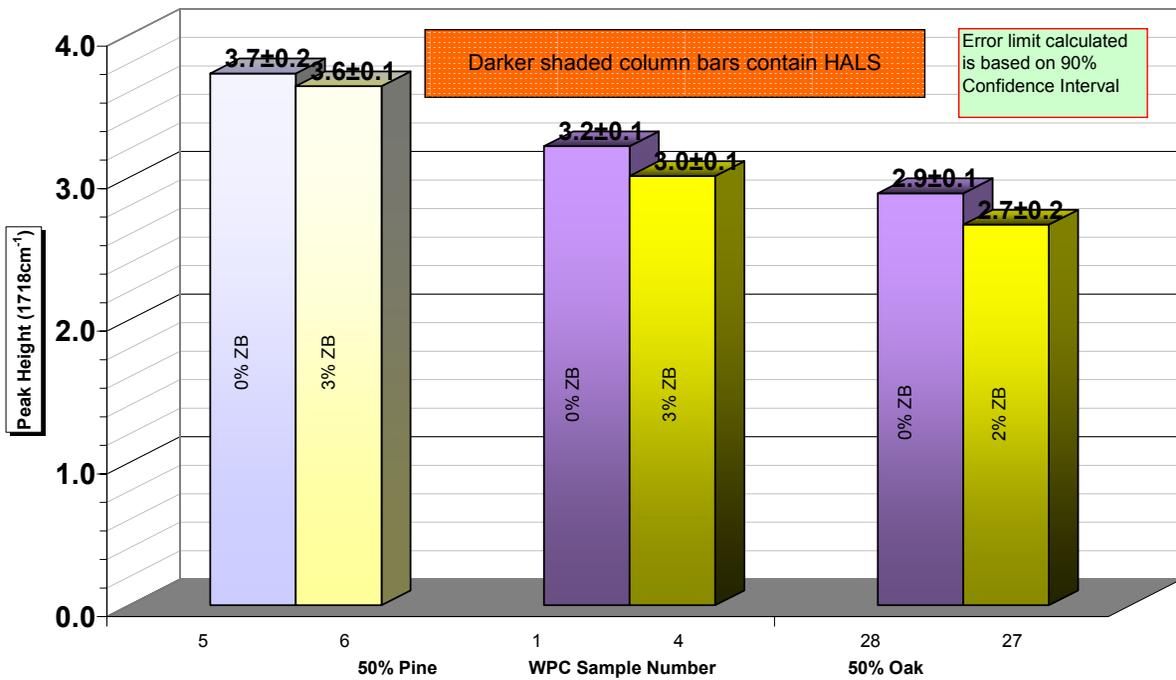


Comparison of non-weathered WPC (A – formulation 27) and weathered samples of WPC (B – formulation 27, and C – formulation 28) exposed to 2000h of accelerated weathering (condition a)

**PHOTO-OXIDATION COMPARISON BETWEEN POLYETHYLENE
IN WPC AND PE FILM (ATR [SPLIT PEA]) After 100h QUV Exposure (condition a)**



**PHOTO-OXIDATION OF POLYETHYLENE IN WPC
WITH AND WITHOUT HALS AND ZB (ATR [SPLIT PEA])
after 2000h QUV Exposure (condition a)**



TREND IN WPC ACIDITY (pH) VS. ZINC BORATE CONTENT

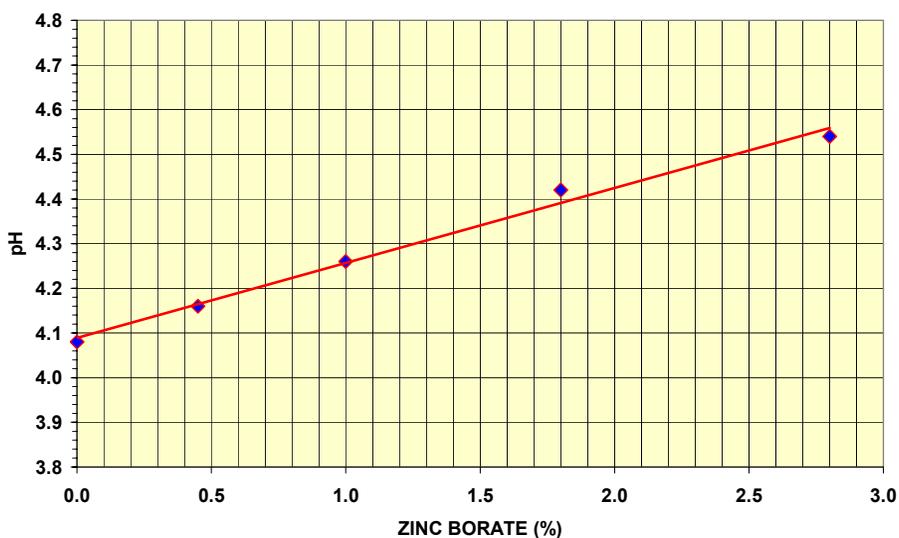
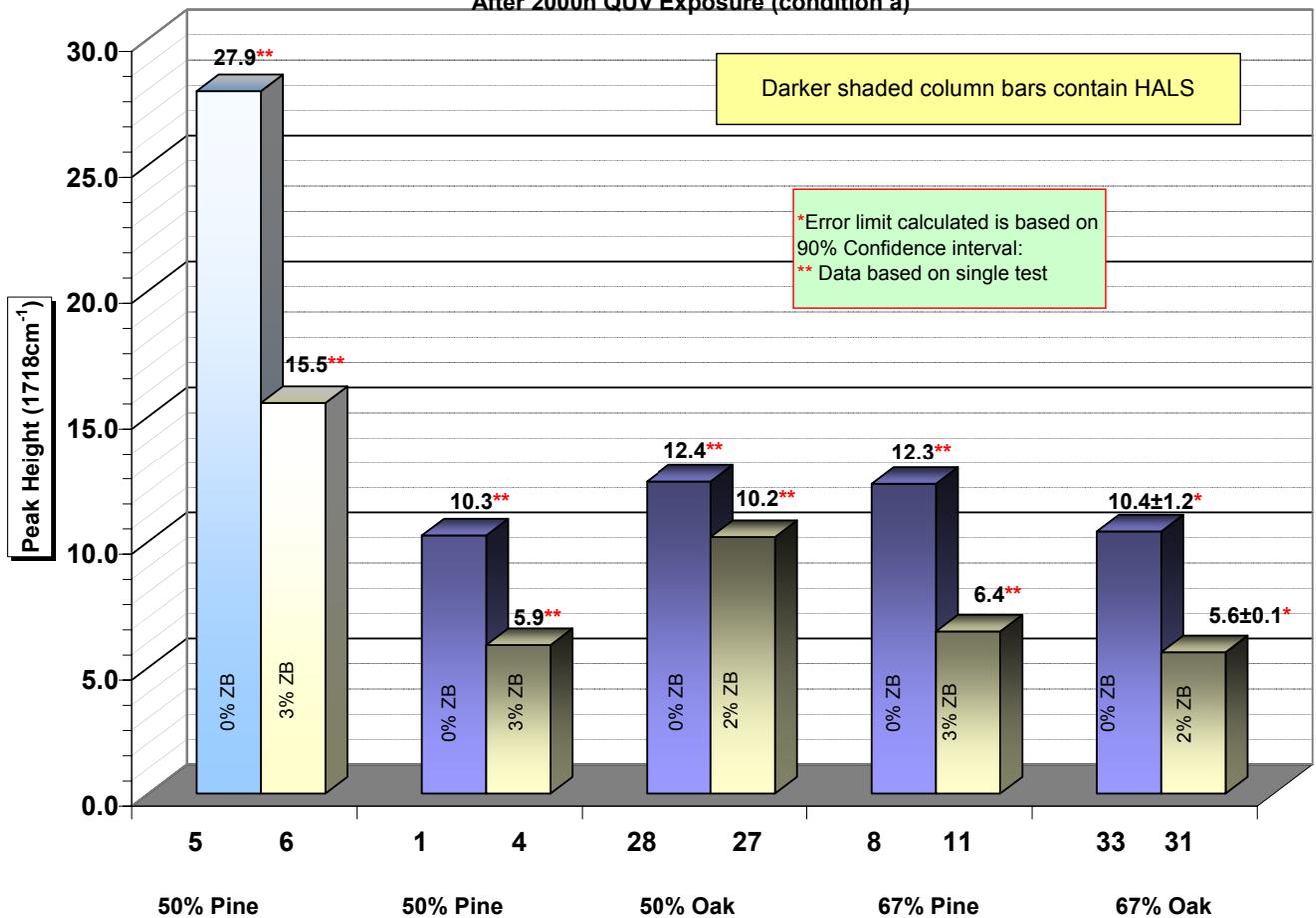
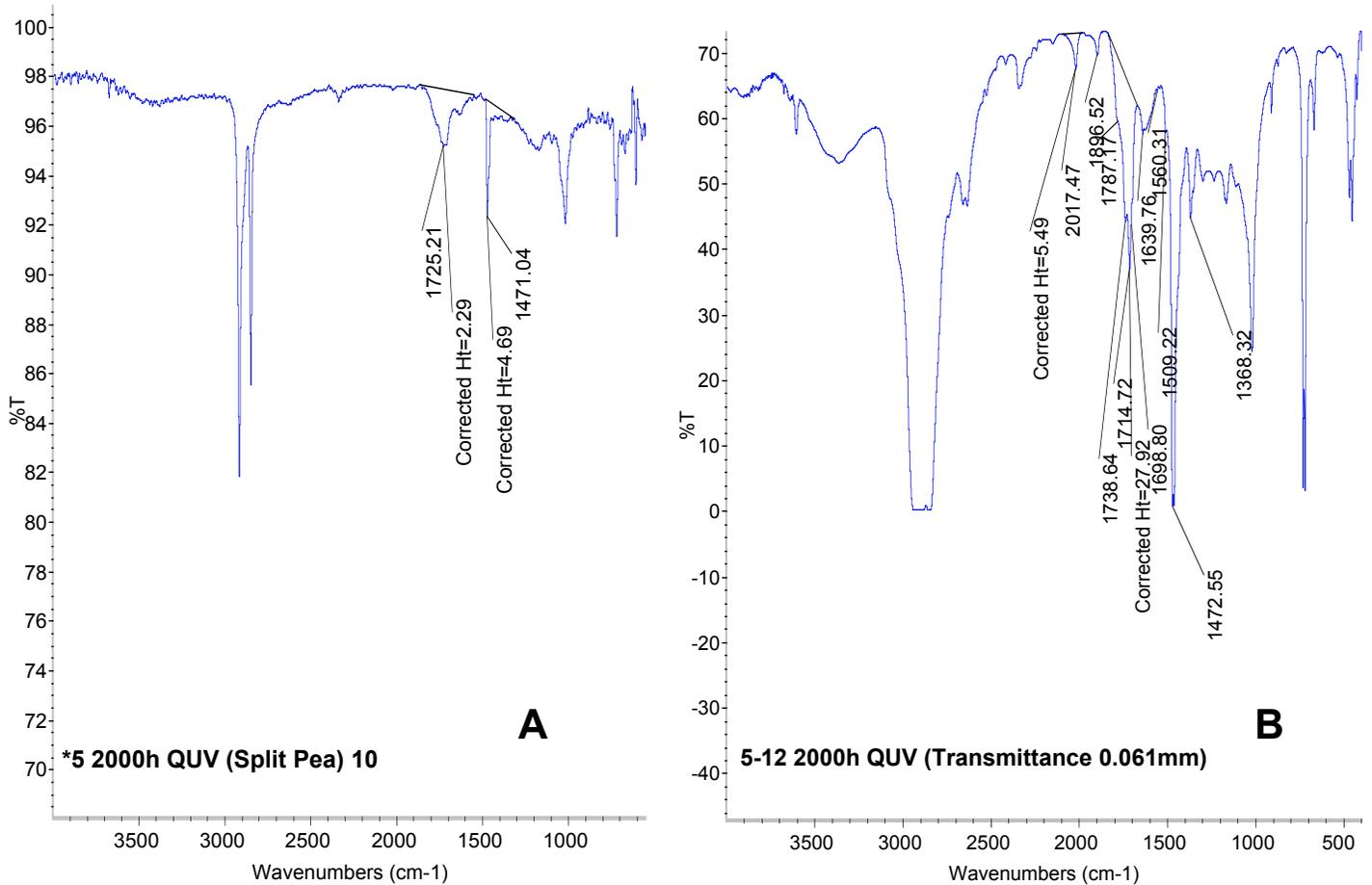


PHOTO-OXIDATION OF POLYETHYLENE IN WPC WITH AND WITHOUT HALS AND ZB

After 2000h QUV Exposure (condition a)



EXAMPLES OF INFRARED SPECTRA OF WPC USED FOR QUANTITATIVE EVALUATION OF MATERIALS PHOTO-OXIDATION



A – ATR spectrum of the surface

B – Transmittance spectrum of the recovered polymer

PHOTO-OXIDATION OF POLYETHYLENE FILMS WITH ZINC OXIDE AND DIFFERENT LEVELS OF ZB
After 100h QUV Exposure (condition b)

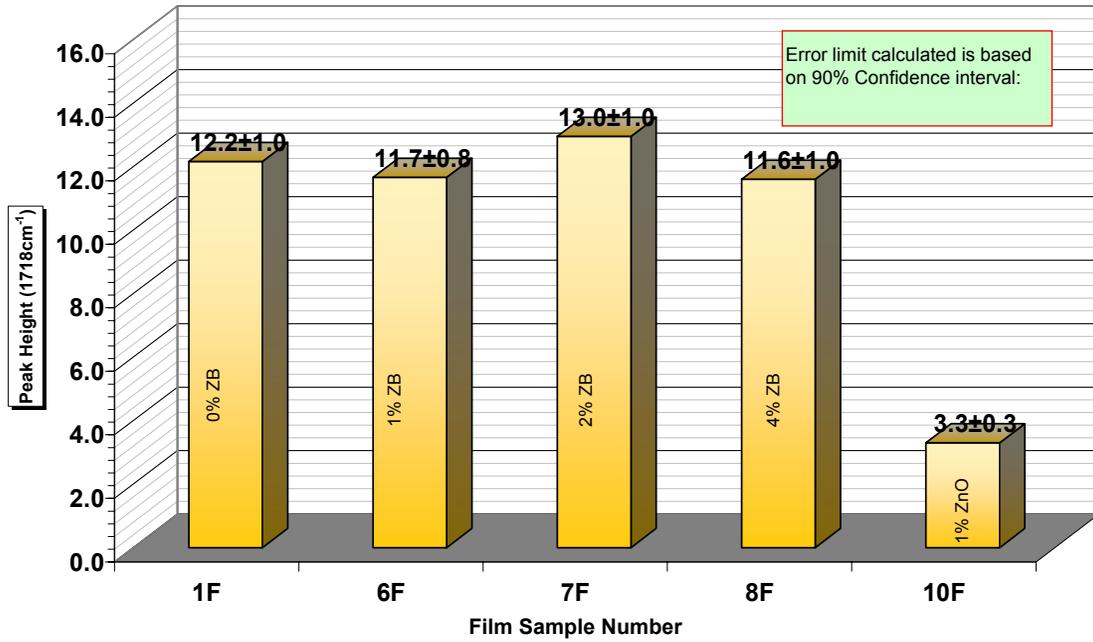
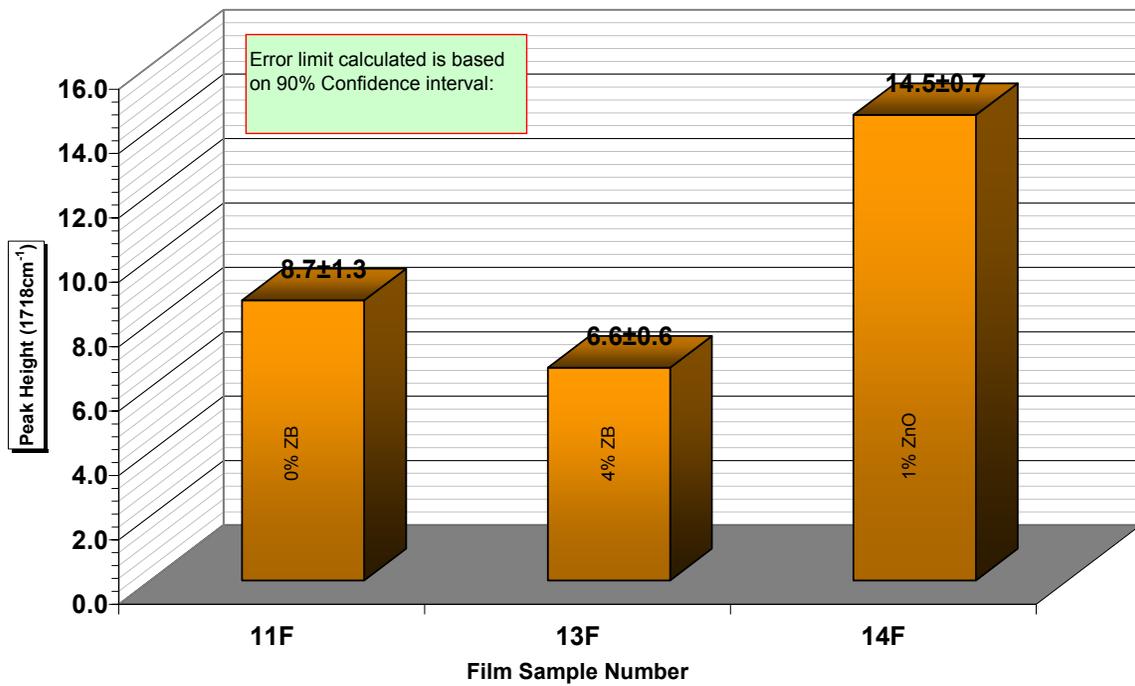
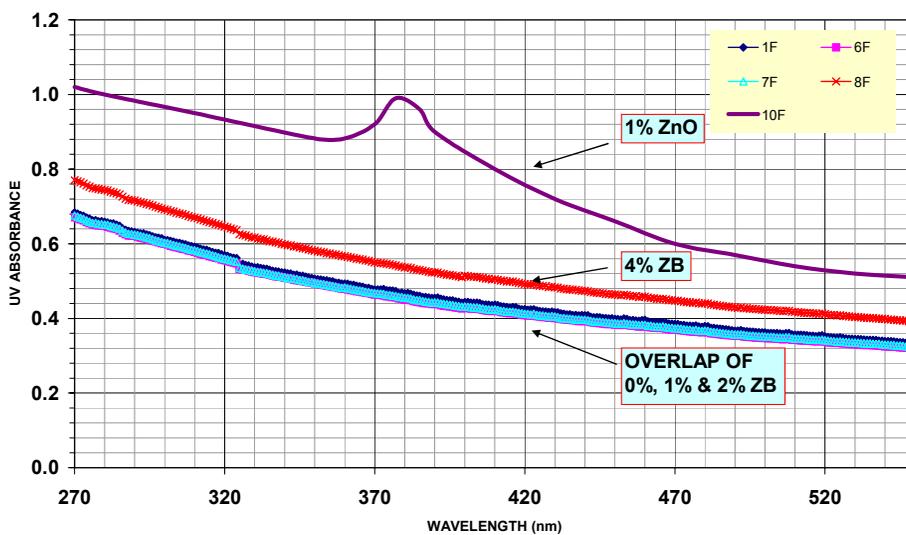


PHOTO-OXIDATION OF POLYETHYLENE FILMS CONTAINING HALS WITH ZINC OXIDE AND DIFFERENT LEVELS OF ZB
After 368h QUV and Diluted Sulphuric Acid Exposure (condition c)



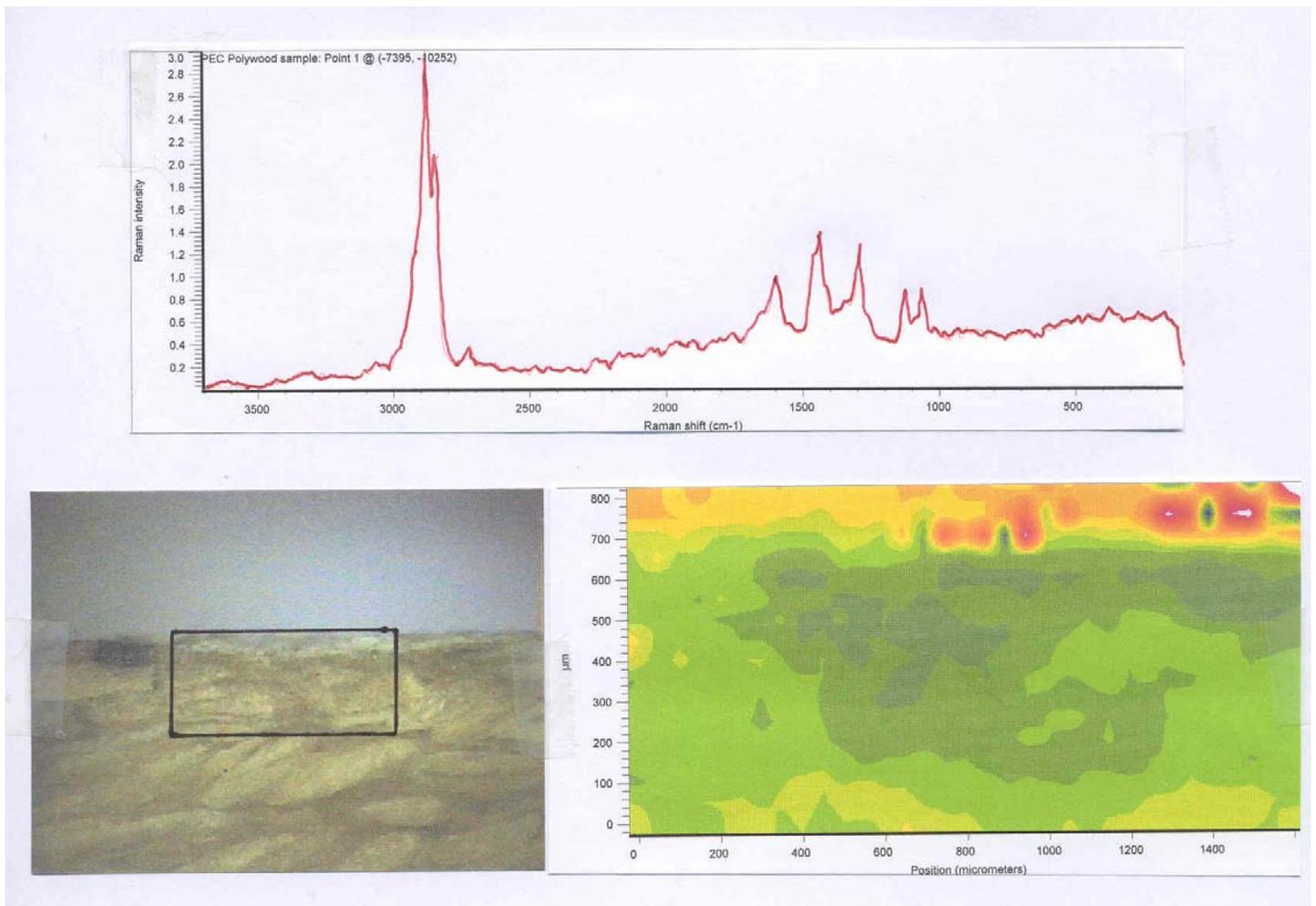
UV ABSORBANCE OF SELECTED POLYETHYLENE FILMS



COLOUR CHANGE (ΔE) AND LIGHTNESS (L^*) OF SELECTED WCP SPECIMENS AFTER 100H, 500H AND 2000H QUV ACCELERATED WEATHERING (condition a)

WPC ID	1	4	5	6	8	11	27	28	31	33		
WOOD %	50 PINE	50 PINE	50 PINE	50 PINE	67 PINE	67 PINE	50 OAK	50 OAK	67 PINE	67 PINE		
ZB %	0	3	0	3	0	3	2	0	2	0		
HALS	+	+	-	-	+	+	+	+	+	+		
COLOUR CHANGE EQUATION LCh (ΔE AND L^*)	100H	(ΔE)	1.0	1.2	2.4	1.5	2.5	4.8	0.8	2.2	3.3	4.8
		(L^*)	69.6	69.6	64.7	64.0	66.9	64.7	67.3	67.1	64.2	66.3
	500H	(ΔE)	1.6	2.1	18.7	21.2	2.0	1.8	4.0	8.8	10.6	10.7
		(L^*)	71.6	71.5	76.0	77.1	71.1	67.9	71.2	73.0	72.1	73.3
	2000H	(ΔE)	5.1	5.4	26.7	26.7	5.0	4.6	7.6	12.6	15.5	15.5
		(L^*)	74.4	74.6	81.5	81.9	73.8	72.4	74.8	76.8	77.0	78.1

RAMAN MICROSCPECTROSCOPY



Raman spectrum of WPC cross-section (sample #5 exposed to 2000h weathering – condition a)
Carbonyl group concentration mapping was generated by computer.
This likely resembles the photo-oxidation pattern in polymers.