UV Stabilization of Wood Plastic Composites with Zinc Borate

***Marek Gnatowski[1], Cecilia Stevens[1], Mark Manning[2]**

1.Polymer Engineering Company Ltd., 110 -3070 Norland Avenue, Burnaby, BC, Canada Email: pecltd@telus.net

2. US Borax, 26877 Tourney Rd. Valencia, CA 91355-1847 Mark.Manning@borax.com

Introduction

Wood plastic composite (WPC) materials are a prime example of composite materials based on natural resources. WPC may contain approximately 30-80% wood in the form of small particles. The remaining 20% or more is thermoplastic resin such as PVC, PP or, most frequently, polyethylene, with additives. In recent years, the market importance of WPC has grown quickly in Europe, Asia, and particularly in North America[1,2] where annual production is reaching 0.5 million tons.

Figure 1. Boardwalk made from wood plastic composites in Everglades National Park in Florida

Due to the presence of both wood and resin, WPC materials are subject to several possible degradation processes. Major factors in WPC degradation are water absorption[3], biological decay, and UV radiation.

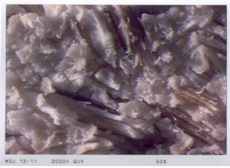

Figure 2. Microscopic picture of weathered surface of unprotected wood plastic composite material. Visible severe plastic breakdown and exposed wood particles.

The use of zinc borate for biocidal purposes in the WPC formulation to eliminate decay and termite damage, and reduce mould and algae growth is well known and documented.[4,5,7]

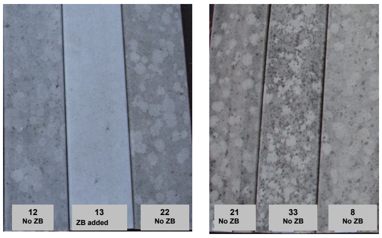

Figure 3. Discolouration of WPC due to fungi growth after 2 years exterior exposure in Vancouver, BC, Canada

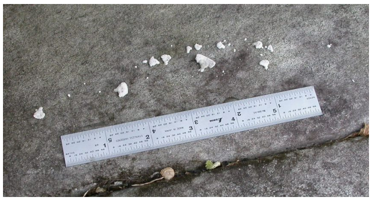

Figure 4. Decay fungi growth on wood plastic composite made without the addition of zinc borate.

This paper presents work that indicates the effectiveness of zinc borate in improving WPC protection against UV degradation, specifically in an acidic environment. WPC is inevitably in an acidic environment due to the presence of wood. Wood is acidic in nature with pH ranging from 3-6. Further acidification of WPC in exterior exposure may occur due to the accumulation of acids from acid rain, and also due to the decay process.

Objective

The objective of the work was to track the progress of the photodegradation process of WPC made using different wood species exposed to an acidic environment.

Experimental

Sample Preparation

Samples of WPC were extruded using a Cincinnati Milicron twin screw extruder with 55 mm conical counter-rotating screw (figure 5).
The composition of WPC materials used for the experiment are shown in table 1.

Figure 5. Cincinnati Milicron twin screw extruder used for extrusion

Table 1. Composition of WPC materials

Materials	Materials Quantity %					
	1	4	5	6	27	28
HDPE[1]	36.0	36.4	45.0	44.3	36.6	36.0
Pine Wood	49.8	47.5	51.0	48.7	-	-
Oak Wood	-	-	-	-	48.3	49.8
UV stabilizer package[2]	9.2	9.1	-	-	9.14	9.2
Zinc borate[3]	-	3.0	-	3.0	2.0	-
Lubricants	3.0	3.0	3.0	3.0	3.0	3.0
Talc	1.0	1.0	1.0	1.0	1.0	1.0

1. B53-35H-001 (Solvay)
2. Tinuvin® 770 (Ciba) 5 pbw, Tinuvin® P (Ciba) 5 pbw,
   metal oxides pigments-15% (Clariant), HDPE (carrier)-75%
3. Borogard® ZB (US Borax)

Sample Exposure

The samples were subjected to QUV exposure under 340 UVA lamps (0.77W/m^2/nm) with cycle of 8h irradiation followed by 4 hours condensation. The accelerated effect of an acid environment was simulated by removing the samples from the weathering chamber every second condensation cycle (e.g. every 24 hours) and soaking them in the H_2SO_4 solution at pH=3 for 2 hours.

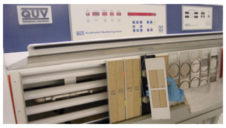

Figure 6. QUV accelerated weathering chamber

Photodegradation Assessment

Photodegradation of polymer binder in WPC samples was evaluated using ATR-FTIR spectroscopy[6-9]. Areas with minimal cellulosic interference were selected for semi-micro analysis. A typical FTIR spectrum of the weathered WPC surface is shown in figure 7. Twenty seven spectra for each sample were collected and averaged for quantitative evaluation. Evaluation of the degree of photodegradation was done by comparison of the normalized intensity of the carbonyl peak at 1718cm^{-1}. The CH_2 deformation vibration band at 1470cm^{-1} adjusted to 100% crystallinity was used as a reference to normalize data in the form of carbonyl index.

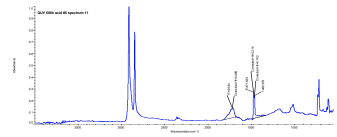

Figure 7. Typical FTIR spectrum of WPC weathered surface

Results

Scanning Electron Microscopy showed distrbution of zinc borate in wood plastic composite material within the binder and near the surface of the wood in the form of well-dispersed small particles a few microns in diameter.

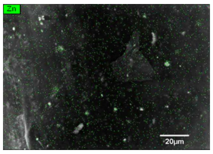

Figure 8. SEM photomicrograph mapping the presence of zinc borate in WPC

pH measurement of sulphuric acid solution after soaking samples of WPC for 2 hours showed significant depletion of hydrogen ions during the initial period of the experiment as shown in figure 9. WPC without zinc borate accepted an acidic environment much faster, while samples containing zinc borate seemed to be buffered and pH did not change as rapidly.

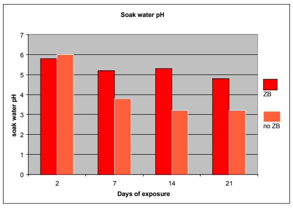

Figure 9. pH of diluted sulphuric acid solution after soaking samples of WPC

Figure 10 compares the carbonyl indices for samples containing pine and oak. Results indicated that WPC made from the pine wood showed more photooxidation reflected as a higher 1718 cm^{-1} absorption band than that of similar samples of WPC made from oak. Also, regardless of wood type, samples containing zinc borate (Borogard® ZB) showed less photooxidation than untreated composites.

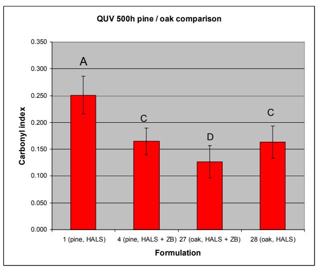

Figure 10. Chart comparing samples containing pine and oak. Statistically significant differences are represented with different letters.

Figure 11 shows a chart comparing the relative intensity of the photooxidation band at 1718 cm^{-1} for wood plastic composites with and without UV stabilizer package after 300 and 500 hours of accelerated weathering. Except for the sample containing the UV stabilizer package without ZB, there is a distinct increase in photooxidation of all of the samples with increased exposure. The presence of the UV stabilizer package reduced photooxidation as expected. Reduction in photooxidation is observed also for all samples containing zinc borate.

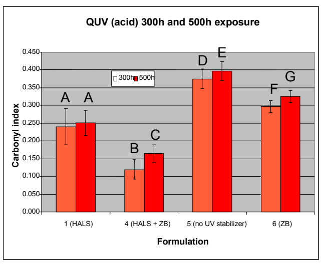

Figure 11. Chart comparing QUV (acid) 300h and 500h exposure samples. Statistically significant differences are represented with different letters.

Comments and Conclusions

- Zinc borate seems to inhibit photooxidation of the polymer in wood plastic composites at low pH.
- Wood species used in manufacturing of WPC seems to affect the photodegradation process of the polyethylene binder.
- Zinc borate seems to be effective in inhibition of photodegradation regardless of wood species present.
- It is expected that some compounds in wood act as powerful photoinitiators in weathering of WPC.
- Zinc borate reacts with these compounds to reduce materials sensitivity to photoreaction.

References

1. J. Morton, J. Quarmley, L. Rossi in proceedings 7th International Conference on Woodfiber-Plastic Composites (and other natural fibres), Forest Products Society, Madison WI, 2003, p. 3
2. Takeyasu Kikuchi in proceedings of Wood-Plastic Composites Conference, Applied Market Information Ltd. Austria Trend Eventhotel Pyramide, Vienna, 2005, New Developments Led by WPC Producers
3. M.Gnatowski in proceedings 8th International Conference on Woodfiber-Plastic Composites , Forest Products Society, Madison WI, 2005, p. 249
4. M. Manning, F. Ascherl, in proceedings 7th International Conference on Woodfiber-Plastic Composites (and other natural fibres), Forest Products Society, Madison WI, 2003, p. 69
5. P. Laks, K. Vehring, S. Verhey, D. Richter in proceedings 8th International Conference on Woodfiber-Plastic Composites, Forest Products Society, Madison WI, 2005, p. 265
6. M. Gnatowski, C. Mah, M. Manning, K. Morris, in proceedings of World Polymer Congress MACRO 2004, Paris, Polymers and Environment
7. W. Lawrence, M. Manning, in proceedings of Wood-Plastics Composites Conference, 2004, Applied Market Information Ltd. Austria Trend Eventhotel Pyramide,Vienna , Material Developments
8. N.M. Stark, L.M. Matuana, *Polymer Degradation and Stability*, 2004, *86, No.1*, 1-9
9. N.M. Stark, L.M. Matuana, *J. App. Poly. Sci.,* 2003, *90*, 2609-17
10. N.M. Stark, L.M. Matuana, C.M. Clemens *J. App. Poly. Sci.*, 2004, *93, No.3*, 1021-30

Acknowledgements

We would like to thank PEC personnel David Lesewick and Beverley Start for their laboratory assistance.

This presentation will be available on the Polymer Engineering Company Ltd. website at www.polymerengineering.ca