Co-Extrusion of WPCs with a Clear Cap Layer to Improve Color Stability

Nicole M. Stark -
USDA Forest Service -
Forest Products Laboratory -
One Gifford Pinchot Drive -
Madison, WI 53726 -

Laurent M. Matuana -
Michigan State University -
Department of Forestry -
126 Natural Resources -
East Lansing, MI 48824 -

Abstract

Wood-plastic composites (WPCs) have been gaining market share in residential construction applications such as lumber for decking, roof tiles, and siding. The durability of these materials in exterior environments is just beginning to be understood. Current research suggests that controlling moisture absorption by the composite is key to improving durability. Methods to improve moisture resistance of WPCs have met with limited success. Co-extrusion involves the simultaneous extrusion of two dissimilar materials as a single profile. A previous study demonstrated that co-extrusion of a base WPC with a clear cap layer positively enhanced water sorption characteristics initially, but weathering cracked the cap layer and caused delamination. Therefore, we investigated co-extruding a stabilized high-density polyethylene (HDPE) cap layer with a base WPC consisting of 50% juniper wood flour, 44% HDPE and 6% lubricant. The HDPE cap layer included combinations of a compatibilizer, nano-TiO_2, and a photostabilizer package. A 2^3 full factorial design was used to determine the formulations of the cap layer. Composite color was monitored and changes were calculated after weathering for 1000 hours in a xenon-arc weathering apparatus. The results suggest that either nano-TiO_2 or a photostabilizer package can be used to prevent cap layer cracking and aid in color retention after weathering. However, statistical models developed suggest that there is a negative interaction when using the two together.

In Proceedings: 4th Wood Fibre Polymer Composites International Symposium: March 30-31, 2009, Bordeaux, France.

Introduction

Advanced biobased composites such as wood-plastic composites (WPCs) represent an emerging class of materials that combines the favorable performance and cost attributes of both wood and plastics [1]. Although decking is the largest application for WPCs in North America, another residential application, siding, has tremendous potential. To enter the siding market, the color stability of WPCs needs to be improved.

The outdoor durability of these materials is just beginning to be understood. There has been work examining degradation of WPCs due to weathering and/or decay. The results demonstrate that degradation in exterior environments occurs in the form of color change, mechanical property loss, and loss in weight. Some of the current research demonstrates that controlling moisture absorption by the composite is key to controlling the degradation that occurs during weathering and fungal attack [2,3]. Therefore it is critical to improve the moisture resistance of WPCs in order to enhance WPC durability and expand into new markets.

Current methods to improve the moisture resistance of WPCs have included changing the morphology of the composite, treating the wood component with acetic anhydride, and incorporating a maleated polyolefin into the composite. Changing the manufacturing technique and/or variables alters the composition of the composite surface, changing the way WPCs degrade [2,3]. This has been shown to improve WPC durability in the short term only. Given enough exposure time this method does not prevent the wood from absorbing moisture. Treating the wood fiber with acetic anhydride results in tremendous improvements in moisture resistance, but requires an extra step to pre-treat the wood fiber, and requires exotic catalysts [4]. This has proven to be too expensive for commercial use. Using a coupling agent to improve moisture resistance is cost-effective; it is added directly during the extrusion process. However it has not been very successful to this date [5].

Another technique that can be used to improve the moisture resistance of WPCs, thereby improving durability, involves coating the WPC surface using co-extrusion. Co-extrusion involves extruding two dissimilar materials into a single profile. Of the more than 30 commercial manufacturers of WPCs, co-extrusion is currently used by at least two; however the cap layer is typically an unfilled plastic pigmented a solid color that hides the wood composite underneath.

This leads to a product that has the appearance of solid plastic, and does not convey a "high-end" feeling.

In a previous study, we used co-extrusion to add a clear cap layer to WPCs [6]. The intent was to allow the beauty of the natural wood color to show through, resulting in a higher-valued, durable product. Water soak data showed that co-extruding a clear cap layer of HDPE over a base WPC consisting of wood flour, HDPE, and a lubricant resulted in enhanced water sorption properties initially. Color change was calculated after weathering. The composite with the HDPE cap layer performed better than the control composite. Although the HDPE cap layer performed better than the control, it was noted that the cap layer cracked during weathering, and some delamination occurred [6]. This would allow pathways for moisture penetration, limiting improvements in the color stability.

The objective of this study was to examine strategies to stabilize the clear cap layer of a co-extruded WPC material, thereby improving color stability. We chose three variables to examine for use in the cap layer. A compatibilizer was used to prevent delamination of the cap layer with the base WPC. Two variables were chosen to protect the cap layer against cracking associated with photodegradation. A nano-sized TiO_2 was chosen to act as a photoblocker without imparting any color, and a photostabilizer package consisting of an ultraviolet absorber and hindered amine light stabilizer was also investigated.

Experimental Methods

Materials and Manufacturing

The materials used to manufacture both the base WPC and the cap layer are listed in Table 1. All materials were used as supplied with exception to the juniper wood flour. The juniper wood flour was manufactured at the Forest Products Laboratory. Juniper chips were sent from land in Utah operated by the U. S. Bureau of Land Management. The chips were hammermilled twice, first using a screen with 13 mm (1/2 in.) openings, then using one with 0.8 mm (1/32 in) openings. Similar to the screening of the pine wood flour, wood flour that passed through a 40 mesh screen but remained on a 80 mesh screen was used to manufacture the composites.

Table 1. Materials used to manufacture WPC composites co-extruded with an HDPE cap layer.

Materials		Supplier	Grade
Base WPC	Juniper Wood Flour	Manufactured at FPL	na
	HDPE	Exxon Mobil (Houston, TX)	AD60-007, 0.73 mfi
	Lubricant	Struktol Company of America (Stow, OH)	TPW 709
Cap Layer	HDPE	Exxon Mobil (Houston, TX)	HD 6605.7, 5 mfi
	Compatibilizer	Struktol Company of America (Stow, OH)	TR 065
	Nano TiO_2	Kemira Pigments (Helsinki, Finland)	UV Titan P580
	Photostabilizer 1	Ciba Specialty Chemicals (Tarrytown, NY)	Chimassorb 2020
	Photostabilizer 2	Ciba Specialty Chemicals (Tarrytown, NY)	Tinuvin 360

The base WPC material consisted of 50% juniper wood flour, 44% HDPE, and 6% lubricant. A 2^3 full-factorial design was used to determine the formulations investigated for the co-extruded cap layer. The formulations for the cap layer are shown in Table 2.

Table 2. Formulations of the cap layer co-extruded over a base WPC material.

Formulation	Compatibilizer[1] (%)	TiO_2[2] (%)	Photostabilizer[3] (%)	HDPE[4] (%)
1	0	0	0	100
2	0	0	0.6	99.4
3	0	1	0	99
4	0	1	0.6	98.4
5	0.5	0	0	99.5
6	0.5	0	0.6	98.9
7	0.5	1	0	98.5
8	0.5	1	0.6	97.9

[1]Compatibilizer TR065
[2]Nano-TiO_2
[3]0.4% Photostabilizer 1 plus 0.2% Photostabilizer 2
[4]HDPE 6605.7

The base WPC material and the cap materials were compounded using a 32-mm compounding twin-screw extruder (D-TEX extruder, Davis Standard, Pawcatuck, CT). For both the base WPC material and the cap layer the raw materials were fed into the main feed throat using a gravimetric feed system. Atmospheric and vacuum vents were used to remove any remaining water vapor or other volatiles. Screw rotation and feed rates were chosen to ensure adequate blending yet keep the melt temperature around 200 ºC (400 ºF) to avoid thermally degrading the wood flour. The melt was forced through a strand die. The strands were then cooled and cut into pellets, which were then dried and used as a feedstock for co-extrusion. The processing conditions are shown in Table 3.

Table 3. Compounding conditions for the base WPC material the cap layers.

Formulation	Zone Temperature (°C)								Screw speed (RPM)	Melt temp. (°C)	Melt pressure (MPa)
	1	2	3	4	5	6	7	Die			
Base WPC	179	179	182	182	185	182	182	188	300	207	4.9
Cap Layer	177	177	177	177	177	177	179	182	200	200	2.4

Composites with a cap layer were co-extruded, i.e., two extruders fed into a single die to produce a single profile, using the pre-compounded pellets. A 32-mm conical counter-rotating twin-screw extruder (C.W. Brabender Instruments Inc.) with a length to diameter ratio of 13:1 supplied the base WPC while a 19.1 mm single screw extruder with a L/D ratio of 30:1 (C.W. Brabender Instruments, Inc.) fed the cap material. Both materials were co-extruded through a die (2.54 cm wide by 0.95 cm thick), cooled in a water bath, and cut to 203 mm (8 in.) length. The processing conditions are shown in Table 4.

Table 4. Processing conditions for extruding the base WPC and for co-extruding the base WPC material with the cap layer.

Sample	Extruder	Temperature (ºC), hopper to die				Screw Speed
		Zone 1	Zone 2	Zone 3	Zone 4	(rpm)
Control	Twin	130	131	135	137	35-40
	Single			Not used		
Cap Layer	Twin	130-135	131-135	134-135	136-138	35
	Single	160-165	155	145-152		1

Testing and Analysis

Weathering

All composite samples were placed in a xenon-arc type light exposure apparatus operated according to ASTM D2565 [7] with borosilicate filters (Weather-Ometer 65-WT, Atlas Materials Testing Technology, Chicago, IL). During exposure, the samples were mounted on a drum that rotated around the xenon arc bulb at 1 rpm. Weathering exposure was a 2-h cycle consisting of 108 min of xenon-arc radiation followed by 12 min of simultaneous water spray and UV radiation. An irradiance sensor was used to measure light intensity for wavelengths from 300 to 400 nm (XenoCal, Atlas Materials Testing Technology, Linsengericht, Germany). The irradiance was monitored and voltage to the bulb was changed periodically in order to maintain a constant irradiance. The samples were weathered for 1000 hours, corresponding with a radiant exposure of 129 MJ/m^2.

Color Analysis

A Minolta CR-400 Chroma Meter (Minolta Corporation, Ramsey, NJ) was used to measure color using the CIELab color system. CIELab is a three-dimensional color space measuring the lightness of the sample (L*) and color coordinates (a* and b*). L* ranges between 0 and 100 (black and white, respectively). An increase in L* means the sample is lightening. The color coordinates a* and b* range from –150 to +150. They are defined as the red/green coordinate, a* (+Δa* signifies a color shift toward red, –Δa* toward green) and the yellow/blue coordinate, b* (+Δb* toward yellow, and –Δb* toward blue). Color was measured for five replicate samples, at two locations on each sample. The change in composite lightness and color was determined using the following equation:

$$\Delta x = x_{final} - x_{initial} \qquad [1]$$

where x represents L*, a* or b*. The initial values were measured before weathering and the final values after weathering.

Total color change (ΔE_{ab}) was determined using the procedure outlined in ASTM D2244 [8]. Using this method ΔE_{ab} is calculated as follows:

$$\Delta E_{ab} = \left(\Delta L^2 + \Delta a^2 + \Delta b^2\right)^{1/2} \quad [2]$$

where ΔL, Δa, and Δb represent the difference between initial and final values of L*, a*, and b*, respectively.

Statistics

An attempt was made to model each property using a full-factorial statistical analysis. In this type of design, selected variables are tested at various levels. In our study, we chose the cap layer formulations based upon a 2^3 full factorial design. This translates to three variables (compatibilizer, nano-TiO_2, and photostabilizer) each added at two levels. The combinations of each of these variables are also included in the design (Table 2). Design Expert 7.0.0 software by Stat-Ease (Minneapolis, MN) was used to design our experiment and analyze the data. The data was then analyzed using ANOVA to generate a model describing the data. The derived equations are reported in terms of coded factors. Coding reduces the range of each factor to a common scale, -1 to 1, regardless of its magnitude. In typical coding, -1 is the lower level of a factor and 1 is the upper level.

Results and Discussion

The initial color values, change in color values after weathering, and calculated total change in color are reported in Table 5. Initially, the lightness value, L*, was similar for all the composites. However, the addition of nano-TiO_2 slightly increased L*. The L* for composites without nano-TiO_2 ranged from 40.9-43.7, while the L* for those containing nano-TiO_2 ranged from 47.3-52.1.

The derived equation describing the relationship between the initial L* and the variables in the cap layer (in terms of coded factors) supports the relative importance of TiO_2 in the cap layer.

$$L^*_{initial} = 45.85 + 1.20(Comp.) + 3.32(TiO_2) - 0.0097(PS) + 0.71(Comp.)(PS) \quad [3]$$

All of the main factors and the significant interaction are included in Equation 3. The photostabilizer effect on L* was not significant, but it was included in the model to maintain hierarchy. The relative effect of each factor in this equation is expressed in by its coefficient and algebraic sign. As Equation 3 clearly indicates, nano-TiO_2, was the most important additive in the cap layer that influenced initial lightness.

The chromaticity coordinate, a*, was also similar for all the composites initially. The chromaticity coordinate b* appeared to change with the addition of nano-TiO_2. It ranged between 14.0 and 15.9 without nano-TiO_2 and between -4.6 and 6.3 with nano-TiO_2. These results suggest that although nano-sized TiO_2 was chosen to maintain a clear cap layer, it did slightly change the color of the composites.

Table 5. Color data and calculated changes in color values and total color for the WPC composite and the formulations co-extruded with a cap layer.

Formulation			Initial Color Values			Change after Weathering			
Comp.	TiO_2	PS	L*	a*	b*	ΔL*	Δa*	Δb*	ΔEab
Control			42.0	9.1	15.9	39.7	-7.1	-12.0	42.0
			(2.0)	(0.1)	(0.6)	(4.5)	(0.8)	(1.6)	(4.8)
-	-	-	42.8	9.1	15.0	24.8	-3.7	-1.0	25.1
			(0.7)	(0.3)	(0.4)	(3.5)	(1.0)	(1.3)	(3.6)
-	-	+	40.9	8.2	12.5	21.0	-2.4	5.4	21.9
			(1.4)	(0.2)	(1.1)	(1.9)	(0.5)	(1.5)	(7.2)
-	+	-	47.3	7.6	-0.1	19.2	-1.9	9.6	21.6
			(1.2)	(0.3)	(2.3)	(2.1)	(0.6)	(1.5)	(1.5)
-	+	+	47.6	8.0	6.3	19.5	-2.5	5.9	20.6
			(1.2)	(0.2)	(2.2)	(1.7)	(0.5)	(1.4)	(1.4)
+	-	-	43.7	8.8	14.5	25.2	-3.8	-1.2	25.5
			(1.0)	(0.2)	(0.8)	(2.5)	(0.5)	(1.5)	(2.5)
+	-	+	42.7	8.6	14.0	17.7	-2.3	2.8	18.2
			(0.7)	(0.2)	(0.8)	(3.9)	(0.6)	(1.9)	(4.0)
+	+	-	49.6	7.6	0.7	19.3	-2.2	8.3	21.1
			(1.0)	(0.2)	(1.4)	(1.3)	(0.4)	(1.2)	(1.6)
+	+	+	52.1	7.0	-4.6	16.5	-1.0	12.3	20.6
			(1.3)	(0.1)	(1.2)	(0.9)	(0.2)	(1.3)	(1.2)

Numbers in parentheses represent one standard deviation

Lightening after weathering, indicated by a positive ΔL*, is an undesirable characteristic of WPC weathering. In our study, all of the composites lightened after weathering. However, the largest increase in L* occurred for the control composite, without a cap layer. Adding a cap layer did decrease lightening (i.e., smaller ΔL*), and the additives also had a positive effect on

lightening. Weathering also caused a decrease in Δa* for each of the composites, indicating a loss in the red value. This can contribute to color fade, which is also an undesirable characteristic of WPC weathering. When a clear cap layer was added to the base WPC, the decrease in a* was smaller. Weathering the base WPC resulted in a decrease in b*, or a decrease in the yellow value. Several of the composites with a cap layer also experienced a decrease in b*, however, others experienced an increase. Generally, composites containing either nano-TiO_2 or photostabilizer in the cap layer experienced some yellowing (i.e., increase in b*).

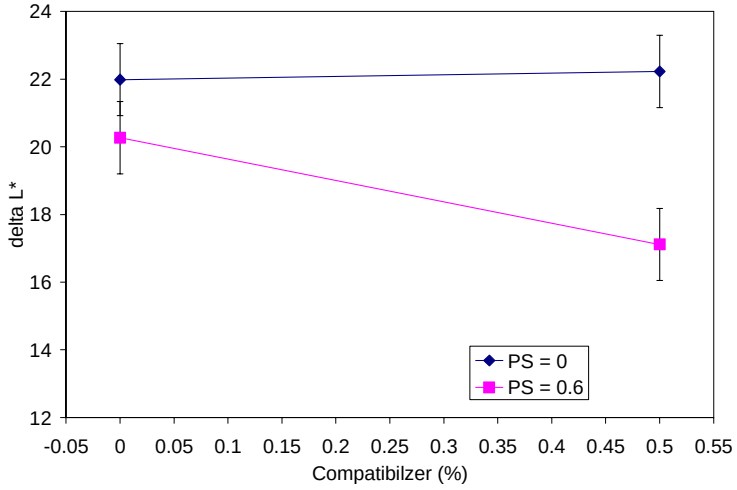
When determining composite degradation we are most often concerned with composite lightening. Therefore we developed a model relating ΔL* with the variables in the composite cap layer. The following equation describes this relationship.

$$\Delta L^* = 20.40 - 0.73(Comp.) - 1.78(TiO_2) - 1.71(PS) - 0.85(Comp.)(PS) + 1.08(TiO_2)(PS) \quad [4]$$

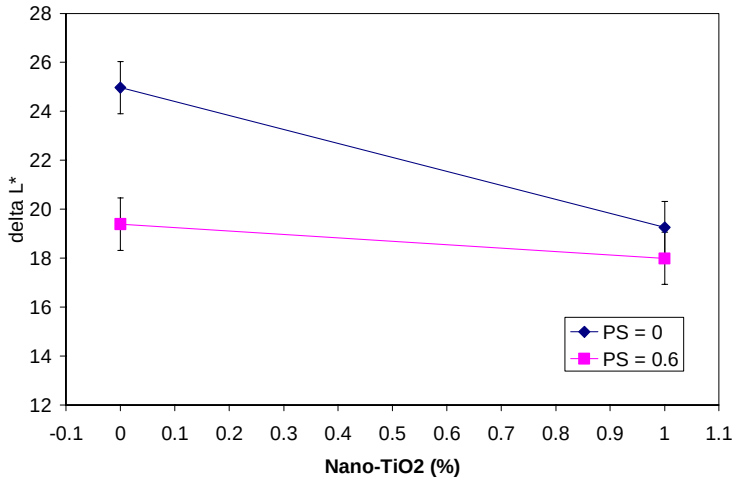
Equation 4 contains all of the main factors and the significant interactions. The effect on ΔL* by the compatibilizer was not significant, but it was included in the model to maintain hierarchy as it appears in an interaction. Each of the main factors had a positive influence on the increase in lightness, indicated by a negative coefficient. The magnitude of the TiO_2 and PS coefficient is similar, suggesting that both contribute equally to decrease composite lightening after weathering.

The interactions of the variables were investigated further. The interaction between the compatibilizer and the photostabilizer is shown in Figure 1a. When the photostabilizer is not included (i.e., PS = 0) the compatibilizer has only a small effect on composite lightening. When the photostabilizer is included (i.e., PS = 0.6) the inclusion of the compatibilizer into the composite has a larger influence on composite lightening. This suggests a synergism between the photostabilizer and compatibilizer. The compatibilizer was added to the cap layer to help prevent delamination between the base WPC and the cap layer. During weathering, the cap layer without the photostabilizer may be cracking, which would allow water penetration through to the base WPC and exacerbate delamination. The addition of the photostabilizer may help prevent cracking, thereby working synergistically with the compatibilizer to prevent degradation.

The interaction between the nano-TiO_2 and the photostabilizer is shown in Figure 1b. When the photostabilizer is not included (i.e., PS = 0) the nano-TiO_2 has a positive effect on decreasing composite lightening. Inclusion of the photostabilizer (i.e., PS = 0.6) lessens the effectiveness of the nano-TiO_2. Although Equation 4 suggests that both the photostabilizer and nano-TiO_2 positively influence composite lightening, the interaction graph shows that effect of nano-TiO_2 is hindered by the addition of a photostabilizer.



(a)



(b)

Figure 1. Variation in ΔL* as a function of the interactions between the: (a) compatibilizer and photostabilizer and (b) nano-TiO_2 and photostabilizer.

The total change in color, ΔE_{ab}, was higher for the WPC composite without the cap layer compared with those that were co-extruded with a cap layer. It was difficult to draw general conclusions regarding the effect of the variables in the cap layer on ΔE_{ab}. Therefore we developed a model to relate the calculated ΔE_{ab} with the variables in the cap layer. This relationship is shown below.

$$\Delta E_{ab} = 21.83 - 0.84(TiO_2) - 1.51(PS) + 1.12(TiO_2)(PS) \qquad [5]$$

Equation 5 includes the significant main variables as well as the significant interaction. The compatibilizer did not significantly influence ΔE_{ab}. It is clear that total color change decreases when either nano-TiO_2 or photostabilizer is included in the cap layer. However, there is an interaction between the two (Figure 2). Similar to the interaction effect on ΔL^*, when the photostabilizer is not included, adding the nano-TiO_2 has a positive effect on ΔE_{ab}. However, when the photostabilizer is included, the nano-TiO_2 is not effective at lowering total color change. This indicates that either nano-TiO_2 or a photostabilizer package can be chosen to protect a clear cap layer of a co-extruded WPC, but they should not be used together.

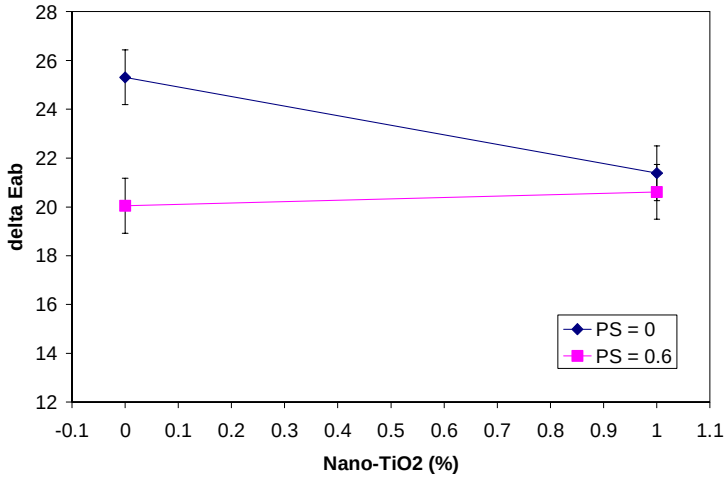


Figure 2. Variation in ΔE_{ab} as a function of the interaction between nano-TiO_2 and photostabilizer.

Summary and Conclusions

It has been shown that controlling moisture is key to improving weathering performance. Previous studies have shown that co-extrusion of a base WPC with a clear cap layer positively enhances water sorption characteristics, but weathering cracks the cap layer and causes delamination. Therefore, we examined the effect of a stabilized cap layer co-extruded over a base WPC on color changes of the composite after weathering. Co-extruded composites were manufactured using a base material of 50% juniper wood flour, 44% HDPE and 6% lubricant. The composites investigated included a control WPC, and composites capped with an HDPE layer including combinations of a compatibilizer, nano-sized TiO_2, and a photostabilizer package. A 2^3 full factorial design was used to determine the formulations of the cap layer.

Adding an HDPE clear cap layer over a WPC composite provided some protection against change in color after weathering. Stabilizing the cap layer provided even further protection. The compatibilizer significantly improved composite lightening (i.e., decreased ΔL^*) only when used in combination with the photostabilizer, suggesting a synergism between the two. The two main variables that significantly improved color stability (i.e., decreased ΔL^* and ΔE_{ab}) were the nano-TiO_2 and the photostabilizer package. Although each was effective, the interaction graphs demonstrated that the two negatively interact with each other and should not be used in concert in a clear cap layer.

Acknowledgements

The authors would like to thank the United States Department of Agriculture, Forest Service for providing funding as part of their Biomass Marketing and Utilization program. The authors also thank Struktol Company of America and Kemira Pigments for the gracious donation of materials.

References

1. - C. Clemons, "Wood-Plastic Composites in the United States, The Interfacing of Two Industries," *Forest Prod J*, 52(6): 10-18, 2002.

2. - N.M. Stark, "Effect of Weathering Cycle and Manufacturing Method on Performance of Wood Flour-High-Density Polyethylene Composites," *J Appl Polymer Sci*, 100(4): 3131-3140, 2006.

3. - C.M. Clemons and R.E. Ibach, "The Effects of Processing Method and Moisture History on the Laboratory Fungal Resistance of Wood-HDPE Composites," *Forest Prod J*, 54(4): 50-57, 2004.

4. - R.M. Rowell, "Chemical modification of agro-resources for property enhancement", in R.M. Rowell, R.A. Young, and J.K. Rowell, *Paper and Composites from Agro-Based Resources*, New York, Lewis Publishers, 351-375, 1997.

5. - S. Panthapulakkal, S. Law and M. Sain, "Effect of Water Absorption, Freezing and Thawing, and Photo-Aging on Flexural Properties of Extruded HDPE/Rice Husk Composites," *J Appl Polymer Sci*, 100 (5), 3619-3625, 2006.

6. - N.M. Stark and L.M. Matuana, "Coating WPCs Using Co-Extrusion to Improve Durability," in proceedings, Coating Wood and Wood Composites: Designing for Durability, July 23-25, 2007, Seattle, WA.

7. - ASTM D2565, "Standard practice for xenon-arc exposure of plastics intended for outdoor applications," ASTM International. Standard Test Methods. West Conshohoken, PA, vol. 8.02.

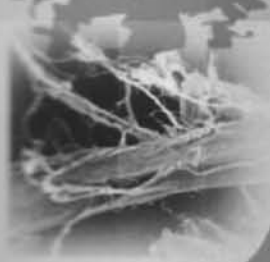
8. - ASTM D2244, "Standard test method for calculation of color differences from instrumentally measured color coordinates," ASTM International. Standard Test Methods. West Conshohoken, PA, vol. 6.01.

FCBA

INSTITUT
TECHNOLOGIQUE

4TH WOOD FIBRE POLYMER COMPOSITES INTERNATIONAL SYMPOSIUM

Natural Fibre to Building and Furniture products: Innovation and Technologies



March 30-31, 2009
Cité Mondiale
Bordeaux – France

Conferences and exhibition

PROCEEDINGS