Durability of Fire-Retarded Wood-Polypropylene Composites Exposed to Freeze-Thaw Cycling

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Abstract

In this study, the effect of accelerated freeze-thaw cycling on the stability of co-extruded polypropylene-based wood-plastic composites containing fire retardants was examined. Five fire retardants, namely melamine, aluminum trihydrate, graphite, zinc borate and TiO_2 were incorporated into the shell layer. The results showed that the tensile strength and modulus of all composites declined by around 11–18 % and 5–21 %, respectively. Fourier transform infrared spectroscopy analysis revealed that melamine and zinc borate leached partly from the surface during weathering. Significant changes in the surface morphology of the weathered composites were observed with a scan electron microscope.

Keywords: wood-plastic composites, fire retardants, freeze-thaw cycling.

Introduction

The market for wood-plastic composites (WPC) is developing fast, projected to reach 1,728.9 kilotons by 2019, with a compound annual growth rate (CAGR) of 10.5 % between 2014 and 2019 (Anon. 2014). The properties of wood-plastic composites are superior to their constituents, wood and plastic, which explains the interest of manufacturers and customers in these materials. In addition, WPC technology makes it possible to produce ecofriendly materials and use recycled plastic and waste wood. Despite the growing popularity of composites, their often inadequate resistance to weathering at outdoor applications remains a concern. Among other impacts, the effect of moisture plays a crucial role in the stability of WPCs in both warm (Stark and Matuana 2006) and cold (Pilarski and Matuana 2005, Wang et al. 2007) environments. Generally, the presence of moisture has a negative influence on the properties of composites due to the swelling of wood particles, which results in fiber/matrix debonding and the formation of microcracks in the matrix (Stark and Matuana 2006, Beg and Pickering 2008). The optimisation of interfacial interaction in the composite provides better water resistance and decreases the loss of properties after weathering (Panthapulakkal et al. 2006, Bergtsson et al. 2007, Turku and Kärki 2013). The method of manufacturing plays an important role in the durability of the composite, so that injection-molded samples are polymer rich and have less void volume than extruded ones, which results in less wettability and improved anti-ageing characteristics (Stark et al. 2004).

Fire retardants (FRs) are widely used to improve the fire resistance of materials (Klyosov 2007). Despite the progress in this technology, there is a lack of information about the influence of FRs on the durability of the composite and the stability of FRs themselves. Fire retardants are usually incorporated into the composite during compounding, and they are not chemically bound to the material. Thus, the FR can leach or wear out of the product during usage, resulting in the increased the sensitivity to fire of the material and causing pollution of the ecosystem as well. It has been reported that halogenated FR, a mixture of polybrominated diphenyl ethers (PBDEs), which are suspected to be endocrine system disrupters, has accumulated in animals, and the concentration levels have been increasing exponentially (Ikonomou et al. 2002). Today, some hazardous FRs are replaced by environment friendly fillers, e.g. metal hydroxides and nitrogen- and phosphate-based ones, thereby reducing environmental and human health impacts. Generally, metal hydroxides have little effect on human health, but moderate neurological risk and skin sensitization have been detected, however. In addition, metals are conservative components, but may change their oxidation state or undergo complexation processes under environmental conditions (EPA 2014). Melamine phosphate has an impact on the human reproductive system (EPA 2014). Release of TiO_2 particles from consumer goods have an ecotoxicological effect on living organisms (Sharma 2009).

In Northern Europe, along with photo-oxidation in warm conditions, the resistance of composites to freezing and thawing actions is an actual issue. It was examined in a separate study (Turku and Kärki 2016) how FRs influence the properties of PP-based WPC under xenon-arc light accelerated weathering. The main objective of this study is to evaluate the effect of freeze-thaw cycles on the tensile properties and surface chemistry of co-extruded WPC with FRs in the surface layer. Fourier transform infrared spectroscopy (FTIR) and scan electron microscope (SEM) are used for the detection possible surface changes.

Experimental

Materials

A polypropylene (PP), Eltex P HY001P (Ineos), with a density of 0.910 g/cm^3 and melt mass-flow rate of 45 g/10 min (230 °C/2.16 kg), was used in the experiments. The coupling agent was maleated anhydride PP (MAPP), Orevac®CA 100 (Arkema). Struktol TPW 113 was used as the lubricant. The pulp cellulose (PC) was delivered by UPM, Finland. Zinc Borate (ZB), $4ZnO \cdot 6B_2O_3 \cdot 7H_2O$, with particle size, d_{mean}= 5 µm, 99% less than 25 µm, was obtained from Chemtura, Switzerland. Melamine, grade F 40, with a solubility of 0.3 g/100 ml, was obtained from EcoChem Technologies, Belgium. Aluminium trihydrate (ATH) with particle size, d_{50} = 1.3–2.3 µm, $d_{90} \leq$ 4.5 µm; a solubility of $1.5 \cdot 10^{-3}$ g/1000 ml, was obtained from Albemarle Corporation, Germany. Graphite, Silvershine, was obtained from Skaland Graphite AS, Norway; and TiO_2 masterbatch, Plastwhite 7038, TiO_2 : PE (polyethylene) = 50 : 50, was acquired from Cabot Clariant, Finland.

Preparation of the composites

Six different composite materials having the same core material and differences in the shell layer were produced. The core layer was produced from a blend with the percentage ratio of WF (wood flour) : PP : MAPP : UV-stab : lubricant : pigment : talc = 63 : 20 : 5 : 1 : 1.5 : 1.5 : 8. The materials and formulations used in the shell are listed in Table 1. A co-extrusion system, a Weber CE 7.2 counter-rotation conical twin-screw extruder, was used to produce the core layer, and a fiberEX extruder to produce the shell layer. The processing temperatures in both extruders were between 174 and 202 °C. The schematic of the co-extrusion profile is shown in Figure 1.

Freeze-thaw cycling weathering

The resistance of the composites to moisture and freeze-thaw actions was tested under cyclic conditions specified by the standard EN 321. Specimens were conditioned to constant mass at (20±2) °C and (65±5) % RH (relative humidity) atmosphere. The test samples were exposed to three cycles, each comprising immersion in water at 23 °C for 70±1 h, freezing at the temperature of –20 °C for 24 h, and drying at the temperature of 70 °C for 70±1 h. The tensile properties of the samples before and after the freeze-thaw experiments were determined according to ISO 527-1.

Table 1. Formulations of the shell layers of the composites. The amounts of the component amounts are given as percent by weight

Composite	Filler					PP	PC	MAPP	Talc	Lubricant	Pigment**
	ATH	Melamine	ZB	Graphite	TiO_2						
Reference						50	34	3	9	3	1
ATH-WPC	10					45	29	3	9	3	1
Melamine-WPC		10				45	29	3	9	3	1
ZB-WPC			10			45	29	3	9	3	1
Graphite-WPC				10		45	29	3	9	3	1
TiO_2-WPC					10*	45	29	3	9	3	1

* - masterbatch (TiO_2 : PE = 50 : 50); PE-polyethylene; **pigment Remafin

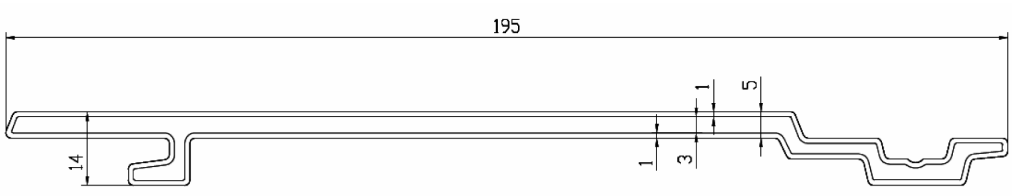

Figure 1. Schematic of the co-extrusion profile

Testing of composites

The tensile properties of the composites were measured in accordance with the standard EN ISO 527-1 in a Zwick/Roell Z020 testing machine. Young's modulus speed, 1 mm min^{-1}, and test speed, 2 mm min^{-1}, parameters were used for test. The cycling weathering tests were carried out with 6 sample replicates. Specimens were conditioned to constant mass at (20±2) °C and (65±5) % RH atmosphere.

FTIR analysis

A Spectrum 100 FTIR spectrometer (Perkin-Elmer, UK) equipped with an attenuated total reflection (ATR) accessory (Perkin Elmer) was used for the composite surface analysis. The spectra were collected by co-adding 20 scans at a resolution of 4 cm^{-1} in the range from 4,000 to 400 cm^{-1}. All spectra were normalized by 2,917 cm^{-1} (C–H band), the specific peak intensity of PP. This peak was selected as the reference peak because it changed the least during weathering.

Microstructure analysis

The microstructure of the composite surface was studied by using a Jeol JSM-5800 LV scanning electron microscope (SEM) at an accelerated voltage of 15 kV. Prior to the analysis, the composite surfaces were covered with a layer of gold with a sputter coater.

Results

The effect of water immersion-freeze-thaw actions on the tensile properties of the composites is depicted in Figure 2. As can be seen, the exposure of the samples to cycling conditions resulted in reduced strength and modulus for all samples. The reduction was by around 11–18 % and 5–21 % for strength and modulus, respectively. The main reason for this can be attributed to water action, which has deteriorated the interfacial interaction in the composite (Pilarski and Matuana 2005, Wang et al. 2007). Water is capable of disrupting interfacial hydrogen bonds, and in addition, hydrophilic cellulosic particles absorb water and swell, which also deteriorates interfacial bonding. Temperature variations during weathering can induce microstructural changes of the polymer, which, however, do not influence the tensile properties significantly (Pagès et al. 1996). Poor stability of WPC exposed to freeze-thaw weathering has been reported previously. Pilarski and Matuana (2005, 2006) reported that flexural properties of high density polyethylene (HDPE) or polyvinyl chloride (PVC) composites filled with different type of wood flour (pine or maple) declined after water immersion-freeze-thaw cycling. Tajvidi and Haghdan (2009) reported that flexural properties WF/PVC composite significantly weakened after cycling. They also report that most changes were at the first cycle and repetition of cycling did not cause significant changes. Adhikary et al. (2010) showed significant loss in flexural properties of the PP- and PE-based (virgin or recycled) WPCs after 12 FT cycles. Durability of rice-hull/PE composites decreased after FT cycling experiment (Panthapulakkal et al. 2006, Wang et al. 2007). Recently, a model for predicting the failure of properties of WPCs subjected to water soak/freeze-thaw cycling has been developed by Srubar (2015).

The structural changes on the composite surface during weathering were estimated by mean FTIR analysis. As can be seen in Figure 3, exposure to the FT cycling procedure caused an increase in the absorbance intensity of groups associated with cellulose, broad signal at 3,100–3,600 cm^{-1} of the O–H stretching and the region between 1,023 and 1,050 cm^{-1} of the C–O groups (Fabiyi et al. 2008, Fabiyi et al. 2011). Their increased intensity

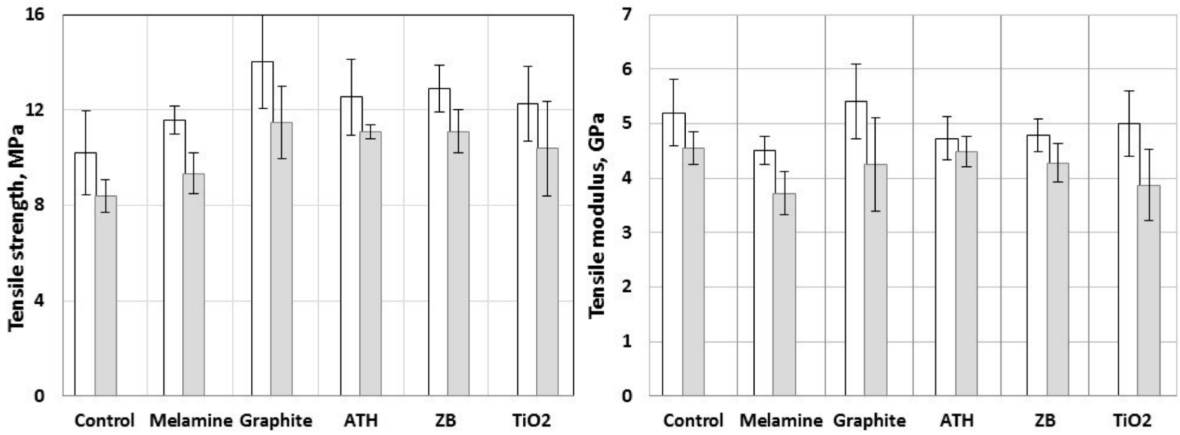

Figure 2. Tensile properties of WPC treated with fire retardants before (unfilled) and after (filled) freeze-thaw weathering

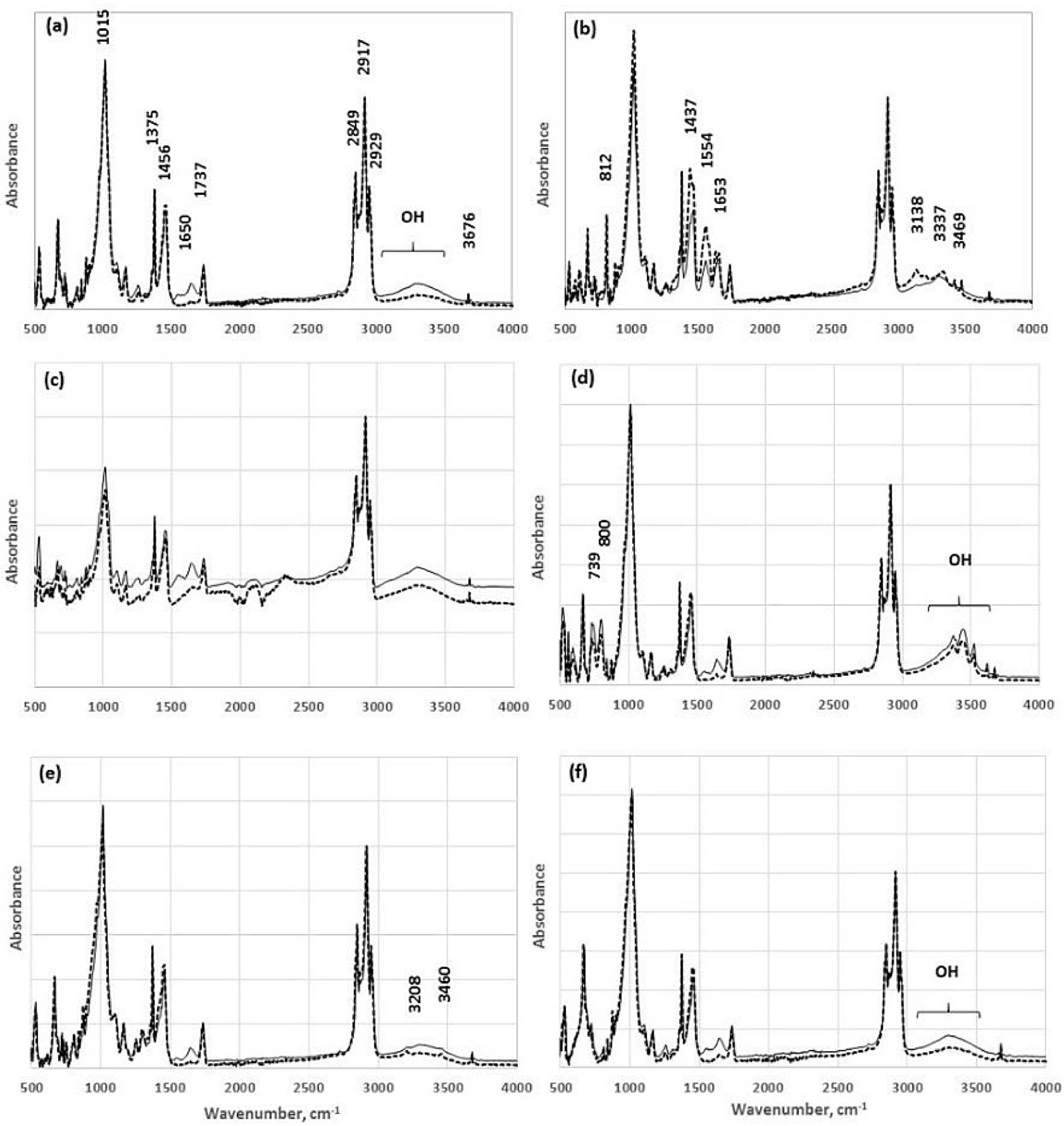

Figure 3. FTIR spectra of the reference (a), melamine-WPC (b), graphite-WPC (c), ATH-WPC (d), ZB-WPC (e) and TiO_2-WPC (f); the dotted line denotes spectra before freeze-thaw cycling weathering, the solid line denotes spectra after the weathering

after the cycling indicates cellulose and PP matrix interfacial debonding as well as exposure of the cellulosic material on the composite surface due to surface cracking. The small peak at 1,650 cm^{-1} before ageing may belong to C=O stretching vibration of α-keto carbonyl in the cellulose or absorbed water (Kazayawoko et al. 1997), which clearly increased after the weathering as well. Wang et al. (2007) also report that the OH peak increased after freeze-thaw cycling.

The accelerated weathering of the melamine-WPC induced noteworthy changes in its infrared spectra (Figure 2b). The presence of melamine on the virgin surface can be identified by the several specific bands. The peaks in the wavenumber regions 3,138–3,469 cm^{-1} are assigned to NH stretching. Melamine *s*-triazine ring bands observed at 813 and 1,554 cm^{-1} correspond to out-of-plane and in-plane vibration of the triazine ring, respectively (Castela et al. 2003). Also, broad bands in the 1,437–1,654 cm^{-1}

region are assigned to CN stretching and NH_2 bending (Mircescu et al. 2012). As can be seen, ageing leads to a decrease of the intensity of most of the peaks attributed to melamine, indicating that melamine was probably leached with water. The durability of functional fillers, i.e. FR, is dependent on their solubility, as the FR can leach from the composite surface during the exposal of the composite in humid conditions (Östman et al. 2001).

The graphite-WPC spectra are shown in Figure 2c. The specific peaks of graphite are aromatic C=C and stretching vibration of different carbonyl groups, at 1,500–1,550 and 1,737 cm^{-1}, respectively (Neha et al. 2012, Panzer and Elving 1975). The increased intensity of the specific to graphite bands is attributed to cracks in the PP layer and the blooming out of graphite particles on the weathered surface.

In the ATH-WPC sample, Figure 3d, the presence of ATH can be identified by peaks at ~700 and 800 cm^{-1} for Al–O and a few peaks at 3,400–3,600 cm^{-1} for hydroxyl groups stretching (Elderfield and Hem 1973, Wefers and Misra 1987). In addition, several unassigned specific peaks in 400–900 cm^{-1} area can be identified in the ATH spectra (Wefers and Misra 1987). The increased intensity of peaks indicates blooming out of FR due to the PP layer cracking. According to the production sheet, ATH has very low water solubility, which could explain its stability at humid conditions, unlike melamine.

Inspection of the ZB-WPC spectra, Figure 3e, shows two ZB-specific peaks, ~3,209 and 3,460 cm^{-1}, attributed to the OH groups. However, the intensity of the peaks decreased after accelerated weathering, suggesting that ZB was affected by the ambient conditions, e.g. leached by water.

The effect of FT cycling on the TiO_2-consisting composite is shown in Figure 3f. Particles of TiO_2 absorb water and are usually covered with hydroxyl groups. The typical infrared spectra of TiO_2 are characterized by bands at 3,000–3,700 cm^{-1}, where free and hydrogen-bonded OH groups can be detected (Allen et al. 2004). It could be noted that TiO_2 was loaded at 5 %, which is a very insignificant amount compared to cellulose. Hence, TiO_2 characteristic bands, which are overlapped with cellulose ones cannot seriously influence the intensity of the OH bands, and, therefore, it is difficult to estimate the behaviour of the oxide during weathering.

In order to support the results of the mechanical tests and FTIR analysis, the surfaces of the composite samples before and after weathering were examined with SEM, and the results are shown in Figure 4. Prior to weathering (Figures 4a-f) the surface PP layer is smooth, whereas after weathering (Figures 4a*-f*), cracks can be found on all of the surfaces of the studied composites. The cracks can have been induced by the expansion/contraction of cellulosic particles due to water absorption/desorption.

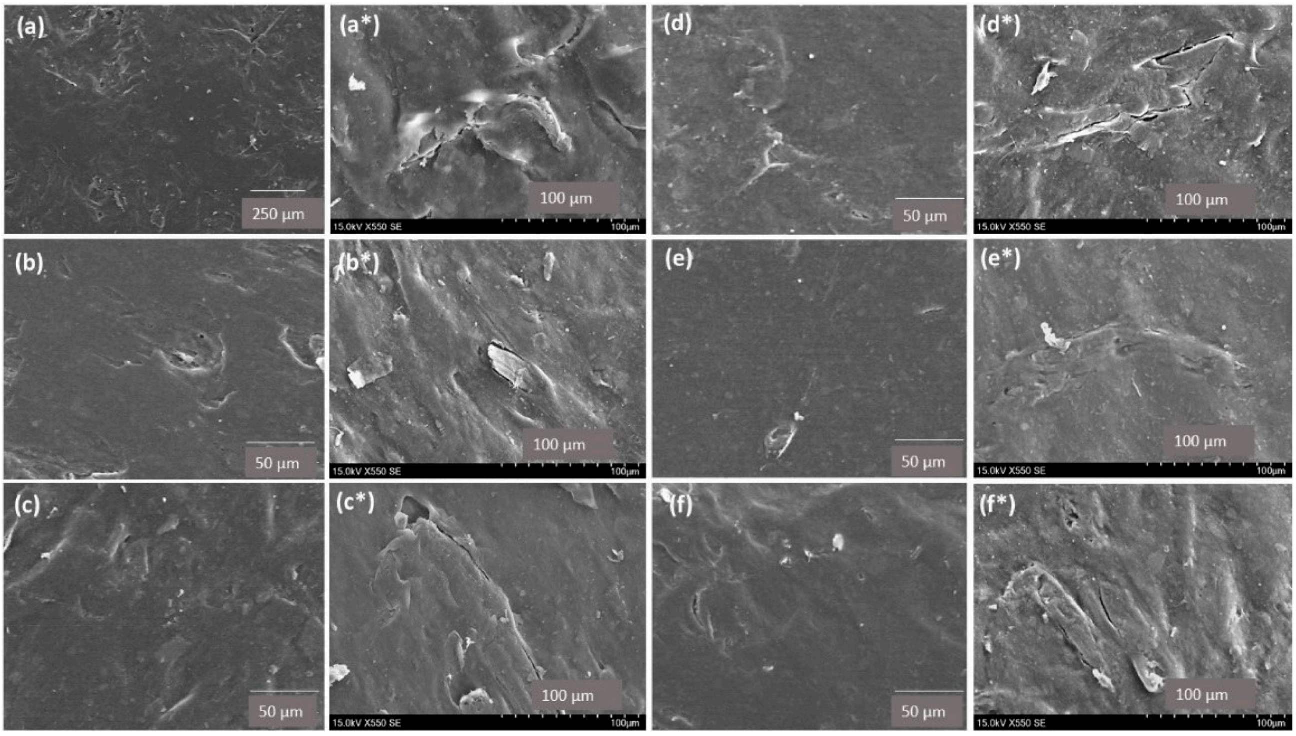

Figure 4. Micrographs of composite surfaces before and after weathering: reference (a), melamine-WPC (b), graphite-WPC (c), ATH-WPC (d), ZB-WPC (e) and TiO_2-WPC (f); asterisk denotes the composite after the freeze-thaw cycling weathering

Conclusions

Wood-plastic composites reinforced with different fillers, namely melamine, graphite, ATH (aluminum trihydrate), zinc borate (ZB) and TiO_2, as well as a control one were exposed to three water soaking-freeze-thaw cycles. It was shown that weathering had a negative influence on the mechanical properties of all of the studied composites, reducing tensile strength (by 11-18 %) and modulus (by 5-21 %) compared to the non-weathered samples. Fourier transfer infrared (FTIR) analysis showed that melamine and ZB were partly leached from the surface. Graphite and ATH, in turn, showed stability during the weathering period. The behavior of TiO_2 could not be estimated adequately due to the fact that its characteristic bands overlap with the cellulose bands. The inspection of the surfaces with a scan electron microscope revealed cracks on the composite surfaces formed during weathering.

One of the important result of this research work is detected leaching of the FRs from the composites during weathering that can lead to increased sensitivity to fire of the material as well as negative effect on the environment. Due to high negative influence on ecosystems and human health of some additives, including FRs (Betts 2002), monitoring stability of reactive component used in material manufacturing becomes actual.

References

Adhikary, K.B., Pang, S. and Staiger, M.P. 2010. Effects of accelerated freeze-thaw cycling on physical and mechanical properties of wood flour-recycled thermoplastic composites. *Polymer Composites* 31(2): 185-194.

Allen, N.S., Edge, M., Ortega, A., Sandoval, G., Liauw, C.M., Verran, J., Stratton, J. and McIntyre, R.B. 2004. Degradation and stabilization of polymers and coatings: nano versus pigmentary titania particles. *Polymer Degradation and Stability* 85(3): 927-946.

Anon. 2014. Wood Plastic Composite Market by Type (Polyethylene, Polyvinylchloride, Propylene, and Others), Applications (Building & Construction Products, Automotive Components, Industrial & Consumer Goods, and Others) and Region – Trends & Forecasts (2014 - 2019). Report Code: CH 2864. Publishing Date: November 2014. By: marketsandmarkets.com. Available from: http://www.marketsandmarkets.com/Market-Reports/wood-plastic-composite-market-170450806.html

Beg, M.D.H. and Pickering, K.L. 2008. Accelerated weathering of unbleached and bleached Kraft wood fibre reinforced polypropylene composites. *Polymer Degradation and Stability* 93(10): 1939-1946.

Bergtsson, M., Stark, N.M. and Oksman, K. 2007. Durability and mechanical properties of silane cross-linked wood thermoplastic composites. *Composite Science and Technol*ogy 67(13): 2728-2738.

Betts, K.S. 2002. Flame-Proofing the Arctic? *Environmental Science and Technology* 36(9): 188-192.

Castela, A.S., Simões, A.M., Davies, G. and Ferreira, M.G.S. 2003. Weathering of coil-coatings: UV radiation and thermal effect. *Revista Metalurgia* 34(36): 167-173.

Elderfield, H. and Hem, J.D. 1973. The development of crystalline structure in aluminium hydroxide polymorphs on ageing. *Mineralogical Magazine* 39: 89-96.

EPA (United States Environmental Protection Agency). 2014. Flame Retardants in Printed Circuit Boards. Updated draft report. December 2014. Prepared by Abt Associates Inc. and Syracuse Research Corporation. 726 p. Available from: http://www2.epa.gov/sites/production/files/2015-01/documents/pcb_updated_draft_report.pdf

Fabiyi, J.S., McDonald, A.G., Wolcott, M.P. and Griffiths, P.R. 2008. Wood plastic composites weathering: Visual appearance and chemical changes. *Polymer Degradation and Stability* 93(8): 1405-1414.

Fabiyi, J.S., McDonald, A.G., Morrell, J.J. and Freitag, C. 2011. Effects of wood species on durability and chemical changes of fungal decayed wood plastic composites. *Composites Part A* 42: 501-510.

Ikonomou, M.G., Rayne, S. and Addison, R.F. 2002. Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian arctic from 1981 to 2000. *Environmental Science and Technology* 36(9): 1886-1892.

Kazayawoko, M., Balatinecz, J.J. and Woodhams, R.T. 1997. Diffuse reflectance Fourier transform infrared spectra of wood fibres treated with maleated polypropylenes. *Journal of Applied Polymer Science* 66(6): 1163-1173.

Klyosov, A.K. 2007. Wood-Plastic Composites. Wiley-Interscience, John Wiley and Sons, Inc., Publication, New Jersey. 702 p.

Mircescu, N.E., Oltean, M., Chiş, V. and Leopold, N. 2012. FTIR, FT-Raman, SERS and DFT study on melamine. *Vibrational Spectroscopy* 62: 165-171.

Neha, B., Manjula, K.S., Srinivasulu, B. and Subhas, S.C. 2012. Synthesis and characterization of exfoliated graphite/ABS composites. *Open Journal of Organic Polymer Materials* 2(4): 74-78.

Östman, B., Voss, A. Hughes, A., Hovde, P.E. and Grexa, O. 2001. Durability of fire retardant treated wood products at humid and exterior conditions. Review of literature. *Fire and Materials* 25(3): 95-104.

Pagès, P., Carrasco, F., Saurina, J. and Colom, X. 1996. FTIR and DSC study of HDPE structural changes and mechanical properties variation when exposed to weathering ageing during Canadian winter. *Journal of Applied Polymer Sci*ence 60(2): 153-159.

Pilarski, J.M. and Matuana, L.M. 2005. Durability of wood flour-plastic composites exposed to accelerated freeze-thaw cycling. Part I. Rigid PVC matrix. *Journal of Vinyl Additives Techno*logy 11(1): 1-8.

Pilarski, J.M. and Matuana, L.M. 2006. Durability of wood flour-plastic composites exposed to accelerated freeze-thaw cycling. II. High density polyethylene matrix. *Journal of Applied Polymer Science* 100(1): 35-39.

Panthapulakkal, S., Law, S. and Sain, M. 2006. Effect of water absorption, freeze and thawing, and photo-aging on flexural properties of extruded HDPE/rice husk composites. *Journal of Applied Polymer Science* 100(59: 3619-3625.

Panzer, R.E. and Elving, P.J. 1975. Nature of surface compounds and surface reactions observed on graphite electrode. *Electrochimica Acta* 20: 635-647.

Sharma, V.K. 2009. Aggregation and toxicity of titanium dioxide nanoparticles in aquatic environment– A review. *Journal of Environmental Science and Health, Part A* 44(14): 1485-1495.

Srubar, W.V. 2015. An analytical model for predicting the freeze-thaw durability of wood-fiber composites. *Composites: Part B* 69: 435-442.

Stark, N.M. and Matuana, L.M. 2006. Influence of photostabilizers on wood flour HDPE composites exposed to xenon-arc radiation with and without water spray. *Polymer Degradation and Stability* 91(12): 3048-3056.

Stark, N.M., Matuana, L.M. and Clemons, C.M. 2004. Effect of processing method on surface and weathering characteristics of wood–flour/HDPE composites. *Journal of Applied Polymer Science* 93: 1021-1030.

Tajvidi, M. and Haghdan, S. 2009. Effect of accelerated freeze-thaw cycling on physical and mechanical properties of wood flour/PVC composites. *Journal of Reinforced Plastics and Composites* 28(15): 1841-1846.

Turku, I. and Kärki, T. 2013. Reinforcing wood–plastic composites with macro- and micro-sized cellulosic fillers: Comparative analysis. *Journal of Reinforced Plastics and Composites* 32(22): 1745-1756.

Turku, I. and Kärki, T. 2016. Accelerated weathering of fire-retarded wood-polypropylene composites. *Composite: Part A* 81: 305-312.

Wang, W.H., Wang, Q.H., Xiao, H. and Morrell, J.J. 2007. Effect of moisture and freeze-thaw cycling on the quality of rice-hull-PE composite. *Pigment and Resin Technology* 36: 344-349.

Wefers, K. and Misra, C. 1987. Oxides and hydroxides of aluminium. Alcoa Technical Paper No. 19, rev. Alcoa Laboratories, Alcoa, USA. 92 p. + i-vi. Available from: http://www.alcoa.com/global/en/innovation/papers_patents/pdf/TP19_Wefers.pdf

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