Improving durability of wood-mixed waste plastic composites with compatibilizers

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Abstract. Wood-plastic composites are often used in applications where they are exposed to weathering effects, e.g. decking, siding and automotive applications, hence weathering properties are important in addition to mechanical properties in terms of usability. In this paper, effect of four different compatibilizers on durability of composites made of wood and mixed waste plastics at two levels of addition was investigated and compared with a reference made without a compatibilizer. Effect of mixing of compatibilizers on performance of the composites was also tested. The mixed waste plastic used consisted of polyethylene and polypropylene originating from commingled construction and municipal solid waste. The findings showed that the durability and weathering resistance of wood-plastic composites made from mixed waste plastics can be improved by using selected compatibilizers. The type and content of the compatibilizer have a notable influence on the effect. The properties of the composites can also be adjusted by hybridizing different compatibilizers, promoting the reuse of mixed waste plastics in wood-plastic composites.

1. Introduction

The global production of plastic materials in 2016 was 335 million tons and the total plastic demand in Europe was 60 m t in the same year. Of all the plastics, different polyolefin (i.e. PE and PP) grades compose 49.1%. In the year 2016, 27.1 million tons of post-consumer waste was collected, of which 31.1% was recycled, 41.6% was consumed in energy recovery but still 27.3% went to landfill [1]. Typical commingled plastic wastes found in post-consumer curbside waste streams are polyolefins (e.g. PP and PE), PS, PET and PVC [2].

The use of recycled plastics in wood-plastic composites (WPC) in order to produce more environmentally friendly materials has also drawn the attention of many researchers [3-10]. In order to decrease the use of virgin plastics made from non-renewable fossil oil, it would be environmentally sustainable to reclaim plastics from waste streams and to recycle them with minimal effort. As WPCs are a mixture of materials by nature, it can be speculated, that reusing mixed waste plastics could be easier within composites than as pure raw materials.

WPCs are commonly used in outdoor applications, such as decking and cladding and in automotive applications [11], where they are susceptible to weathering, i.e. exposure to moisture and UV-radiation. Weathering of WPCs changes their color/appearance [12,13] and mechanical properties [14,15]. As WPCs contain wood and polymers in varying proportions, it also means that they combine the degradation of both materials [16].
Wood in WPCs is mostly responsible for moisture absorption, causing three things that have negative effect on the properties of the composite happen: 1) the interface between wood and polymer breaks down due to swelling and shrinking of wood, 2) microcracking occurs in the plastic, and 3) the wood particles suffer internal fracturing due to restrained swelling [17]. As hydrophilic components (e.g. polyolefin and lignin) degrade on the surface of the composites during weathering, the amount of hydrophilic cellulose increases on the surface. This causes wood-plastic composites to become more susceptible to moisture absorption [18]. Water also accelerates oxidation reactions in composites.

Photodegradation of wood is caused by the degradation of wood’s components (cellulose, hemicellulose, lignin, and extractives), the most relevant of them is lignin breaking down to water-soluble products. The lignin breakdown has multiple routes, which all lead to formation of different chromophoric groups that are the origin of the color change causing photo-yellowing. [19].

For polyolefins, photo-oxidation is the dominating mechanism of UV-degradation, which is result of the absorption of light that initiates formation of radicals causing the oxidation. In addition, impurities, that are not part of the inherent polymer matrix structure, can initiate photo-oxidation [20]. Polymer chain scission, which can be estimated by the increase in the carbonyl index, is accompanied by deteriorating of the mechanical properties of wood-plastic composites. The carbonyl indexes are the most commonly used parameters for assessing the degree of polymer degradation [21].

The performance of composites is not only dependent on the properties of their individual components but also on the interface between the components. The compatibility between the components in WPCs can be improved by using either physical or chemical modification of the polymer or the wood fiber, or by using coupling agents [22]. The effect of different compatibilizers on the weathering resistance of WPCs has been studied, but the focus has not been on utilizing mixed waste polymers, although maleated polyolefins are also used as compatibilizers for polymer blends [23]. It has been reported that the presence of maleated polymers decreased the amount of swelling and moisture pickup in WPCs [24,25]. Also, studies have shown that weathered WPC specimens compatibilized with maleic-grafted PP have notably higher tensile properties, both strength and modulus, than weathered specimens made without compatibilization. Compatibilization also diminishes cracking and deformations of the weathered surface [26]. The use of compatibilizers has also been reported to improve the photostability of WPC significantly [27], in addition to helping retain the mechanical properties [28].

The aim of this study is to evaluate the effect of different compatibilizers on the durability of wood plastic composites made from mixed waste plastics. The effects of different chemical compatibilizers on the weathering resistance of wood - mixed waste plastic composite are studied. In addition, the effect of the addition level of compatibilizers on the weathering performance is evaluated. Changes of surface color, chemistry, morphology, and tensile strength were studied.

2. Experimental

2.1. Materials

The plastic material used in the study was obtained from a regional waste processing plant, Etelä-Karjalan Jätehuolto Oy, Finland. The wastes are composed of material discarded from municipal, construction and commercial sources. The studied plastics were derived from the energy waste component. Only polyolefins were included in the study, as the largest share of plastic waste produced comprises of mixture of both low and high-density polyethylene and polypropylene [29].

The materials were selected manually on the basis of the markings found on the items, so that the composition used in the experiments consisted of 1/3 of PP and 2/3 of PE (of weight), which was found to be the rough average of waste polyolefin plastics found at the site [30]. The PP material consisted mainly of various discarded household goods, e.g. buckets, washing bins, flower pots, garden furniture etc. The PE material was composed mainly of plastic packaging films and bags.

The size of the items was reduced by using an Untha LR630 shredder equipped with a 20mm sieve before agglomerating the composite materials prior to extrusion, with an agglomeration apparatus consisting of a Plas Mec TRL100/FV/W mixer and a Plas Mec RFV-200 cooler.
The compatibilizers used in the study were commercially available. The materials were anhydride modified ethylene copolymer Fusabond N525, chemically modified ethylene elastomer Fusabond N416, anhydride modified polyethylene Fusabond E226, and ethylene copolymer resin Entira EP1754, which were obtained from DuPont de Nemours International Sàrl. According to the manufacturer, all maleated materials had a high maleic anhydride grafting level. Orevac CA100, grafted maleic anhydride functionalized polypropylene, came from Arkema Functional Polyolefins. The mixture of Fusabond N416 and Entira EP1754 (CM), and a mixture of maleated polyolefins (MAM) was fabricated to test the performance of a mixture of maleic crafted PE and PP. The lubricant (processing additive) used was Struktol TPW 113 made by Struktol Company of America, LLC.

The wood material used was spruce (Picea abies spp.) fibers produced with a crusher/shredder Untha LR630, and the particle size was reduced further by using a hammer mill Akron Nirvana FH 64-4-75 equipped with a 2mm sieve, resulting in mean particle size (L/d) of 2.1/0.4 (mm). The naming and compositions of the prepared materials are shown in Table 1.

| Name   | Fiber | Plastic | Compatibilizer type and portion | Lubricant |
|--------|-------|---------|--------------------------------|-----------|
| NC     | 57%   | 40%     | None, 0%                       | 3%        |
| N525-3 | 54%   | 40%     | Fusabond N525, 3%              | 3%        |
| N525-7 | 50%   | 40%     | Fusabond N525, 7%              | 3%        |
| N416-3 | 54%   | 40%     | Fusabond N416, 3%              | 3%        |
| N416-7 | 50%   | 40%     | Fusabond N416, 7%              | 3%        |
| CM-3   | 54%   | 40%     | 2/3*Entira EP1754 + 1/3*Fusabond N416, 3% | 3%        |
| CM-7   | 50%   | 40%     | 2/3*Entira EP1754 + 1/3*Fusabond N416, 7% | 3%        |
| MAM-3  | 54%   | 40%     | 2/3*Fusabond E226 + 1/3*Orevac CA100, 3% | 3%        |
| MAM-7  | 50%   | 40%     | 2/3*Fusabond E226 + 1/3*Orevac CA100, 7% | 3%        |

2.2. Composite and test specimen production

The materials of the composites were agglomerated using a Plas Mec Combimix-RV/100/200/FV/W system. The agglomerate was then extruded into a profile using a Weber CE 7.2 conical counter-rotating twin screw extruder and then cut to test method specific samples. The main extrusion parameters were: Screw speed 14 rpm, Melt temperature 172°C and Melt pressure 2.6 MPa.

2.3. Determination of properties

Resistance to weathering was determined according to standard EN 15534-1:2014. A Q-Sun Xe-3 HS (Q-Lab Corporation, USA) test chamber equipped with a xenon-arc lamp was used in the accelerated weathering testing. The total exposure time was 500 hours. The exposure cycle consisted of 102 min of light exposure followed by 18 min of simultaneous water spray and light exposure, as described in EN ISO 4892-2:2013, Cycle 1. The change in the color of the composites during weathering was measured with a Minolta CM-2500d spectrophotometer (Konika Minolta Sensing Inc., Japan) of 6 replicate specimens. The CIELAB color system was used to measure the surface color in L* a* b* coordinates per ISO 7724.

The total color change $\Delta E$ was calculated by using equation (1):

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

where $\Delta L$, $\Delta a$ and $\Delta b$ represent the difference between the initial values and the values after the exposure.

The microstructures of the composite surfaces were studied by using a Hitachi SU3500 scanning electron microscope (SEM) with 10 kV acceleration voltage under the vacuum of 100 Pa.

Fourier-transform infrared (FTIR) spectroscopy was used to determine changes in the surface chemistry of the composites caused by exposure to accelerated weathering. The analysis of the surfaces of the composite specimens was performed using a PerkinElmer Frontier FTIR spectrometer. The scans were performed at a resolution of 4 cm$^{-1}$ from 4000 to 500 cm$^{-1}$ of 6 separate replicates per
material. The peak absorbance at 2916 cm$^{-1}$, which corresponds to asymmetric stretching of methylene groups, was used for normalization, as it changed the least during weathering. For quantifying the data, baseline corrected peak absorbance values were used. The degradation of the composites was evaluated by using the carbonyl index, which was calculated by using the following equation (2):

$$\text{Carbonyl Index (acids)} = \frac{A_{1715}}{A_{2916}} \quad (2)$$

where $A$ denotes the absorbance at specific wavenumber noted in the subscript.

The effect of weathering on the mechanical performance of the materials was determined according to standard ISO 527-2/1A; tensile strength, by using a Zwick-Roell Z020 universal testing apparatus. A minimum of 8 specimens per material were investigated. Statistical analyses (t-tests for significance) were performed using Statgraphics Plus 4 software.

3. Results and discussion

3.1. Effect of weathering on color

The effect of accelerated weathering on the appearance of the composites was evaluated by determining the total color change of the surface of the materials. The color change was notable in all cases and was exhibited generally as bleaching, i.e. significant changes were found in color component $L$ (lightness). The analysis showed that the color of the composite made without compatibilizers changed initially during weathering fastest, along with MAM-3. Distinctively different behavior compared to the rest of the materials could be observed with material N416-7, which retained its color well up to 300 hours. After 500 hours of exposure, the smallest change was found in material N416-3. The development of color change over time is shown in Fig. 1.

![Figure 1. Color change over the 500h of accelerated weathering.](image)

3.2. Surface structure

The surface structure of the composites after 500h of accelerated weathering was inspected by using SEM. The effect of weathering was typically cracking of the surface and exposure of wood fibers, both caused by the degradation of polymers and repeated swelling and shrinking of the fibers caused by wetting and drying during the accelerated weathering test. The manifestations of the phenomena are shown in Fig. 2.
Initially, the surfaces of the materials appeared relatively similar. On the reference material, more wood fibers appeared close to the surface, yet seeming to be covered by a thin layer of polymers. During the 500h of weathering, the fibers in the reference were exposed in plenty. Maleic grafted compatibilizers have been found to improve the surface integrity of composites exposed to accelerated weathering [26]. Composite N416-7 with the higher 7% compatibilizer content retained its surface integrity the best and the cracking of the plastics matrix was less severe. In general, a higher addition level of compatibilizers resulted in better surface integrity after the weathering.

3.3. Surface chemistry
The FTIR spectra covering carbonyl region (1670-1820 cm\(^{-1}\)) of all the materials are shown in Fig. 3.
The FTIR spectra showed a clear appearance of a peak/shoulder around 1715 cm\(^{-1}\), which indicates formation of carboxylic acids during the accelerated weathering test. No strong indication of carboxylic acids/ketones was present in the non-weathered specimens at 1715 cm\(^{-1}\), but a notable peak was found around 1736 cm\(^{-1}\), suggesting that the reclaimed waste polymers had already aged before the testing and/or degraded thermally during materials processing, or contained impurities [30,31]. Especially the CM materials showed a notable peak at 1736 cm\(^{-1}\) prior to weathering, particularly the material containing 7% of compatibilizer - it had an initial absorbance peak even with MAM-7 after weathering. This peak appeared to be present only in the CM materials, which contained ethylene copolymers without maleic grafting. In addition, a peak in the range of 1730-1734 cm\(^{-1}\) can be attributed to stretching of C=O in cellulose after oxidation [32], so the peak can be a result of various components.

The carbonyl indexes were calculated by using equation 2, and are shown in Fig. 4 with standard deviations. With all materials, carbonyl formation during weathering was significant. A statistically significant difference between the materials was only found between the reference NC and MAM-7 after weathering. This suggests that compatibilization with maleic grafted agents does not in general have strong influence on the UV-inflicted polymer degradation in composites, which is in agreement with the findings of Ratanakamnunt and Aht-Ong [33].
3.4. Mechanical performance

The effect of artificial weathering on the mechanical properties of the composites was evaluated by measuring the tensile strength before and after 500h of exposure. In general, accelerated weathering did not have a remarkable effect on the tensile performance of the composites. The biggest change was recorded with material N525-3, 10.4%, but the change was not statistically significant.

The tensile properties depend on the stress transfer capability within the composite system, and the interface between the wood fibers and polymer matrix is crucial. Repeated swelling and shrinking of wood fibers caused by wetting and drying in weathering testing break and weaken the structure of the wooden counterpart in the polymer matrix [17]. Also bonding between the wood and the polymer matrix is exposed to severe stress. Anyhow, the findings show that compatibilizers have notable effect on the mechanical performance of wood-mixed waste composites, and hybridization of different compatibilizers led to best results. The tensile strengths are presented in Fig. 5.
4. Conclusions
The findings indicate, that compatibilizers have a notable effect on weathering durability of wood-plastic composites made of mixed-waste plastics. In case of color change, notably improved short-term color retention was found with material N416-7 and best longer term performance with N416-3.Compatibilizers can also improve the retaining of the surface integrity of composites exposed to water spray and UV radiation, thus reducing pathways to moisture absorption, especially at addition levels over 3%. The mechanical strength of composites can be notable improved by using selected compatibilizers or hybridized compatibilizers. However, weathering did not have notable effect on strength of composites, hence type and amount of compatibilizers was not significant either.

It was found in the study that the performance and durability of wood-mixed waste plastic composites can be improved by using selected compatibilizers. In general, an addition level higher than 3% was needed to achieve a significant impact. Hybridizing different compatibilizers may also be used to achieve better performance than by using a single additive, which also creates an opportunity for tailoring and optimizing the properties of WPCs. These factors promote the recycling and reusing of waste plastics in a practical manner as a raw material for WPC. Further studies would be beneficial to evaluate the potential of the hybridization of different compatibilizers and to determine the optimum, resource-wise dosage for enhancing wood - mixed waste plastic composites.

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