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Durability and mechanical properties of silane cross-linked wood thermoplastic composites

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Abstract

In this study, silane cross-linked wood–polyethylene composite profiles were manufactured by reactive extrusion. These composites were evaluated regarding their durability and mechanical properties in comparison with two non-cross-linked wood–polyethylene composites. An addition of only 2% w/w of silane solution during manufacturing was enough to achieve almost 60% degree of cross-linking after curing. The cross-linked composites showed flexural toughness superior to the non-cross-linked composites. The cross-linked composites also absorbed less moisture during a boiling test in water and this was an indirect evidence of improved interfacial adhesion. After accelerated weathering for 1000–3000 h the general trend was a decrease in flexural modulus and strength of both the non-cross-linked and cross-linked composites. The decrease in modulus seemed to be lower for the cross-linked composites while the decrease in strength seemed to be higher compared to the non-cross-linked composites. Weathering also resulted in a considerable colour fading of the composites. Water absorption–freeze–thaw cycling decreased the flexural modulus of non-cross-linked composites considerably while there was no statistical decrease in modulus for the cross-linked composites. There was only an insignificant decrease in strength for the composites after the water absorption–freeze–thaw cycling.

Keywords: A. Polymer–matrix composites (PMCs); B. Mechanical properties; B. Durability; E. Extrusion; Cross-linking

1. Introduction

The use of wood based material, such as wood fibres and flour, as reinforcement for thermoplastics has gained significant interest during the last decade. Wood fibre is an interesting reinforcement due to its low cost, abundancy, renewability, low specific gravity and high specific strength and stiffness [1–3]. Wood plastic composites (WPC) have been on the market for more than 10 years now and mainly been used in building and automotive applications. The use of these materials has shown that the main problems are the durability, toughness and long-term load performance.

Although the durability upon weathering of WPC is generally superior to un-treated wood there are still some challenges to be solved. Accelerated weathering studies of the composites have shown colour changes and loss in mechanical properties upon weathering. The colour change of WPC has mainly been ascribed to the effect of ultraviolet (UV) radiation [4–10]. UV light can lead to photodegradation of both the polymer–matrix and the wood in the composites. The main reason for colour fading of WPC has been attributed to the wood component [6,7,9]. However, neat high-density polyethylene also showed colour fading after 2000 h of xenon arc (UV, visible and IR) radiation although the degree of fading was almost nine times lower than in the corresponding WPC [6]. In wood, lignin is responsible for most of the light induced yellowing although there is a small contribution from the other wood

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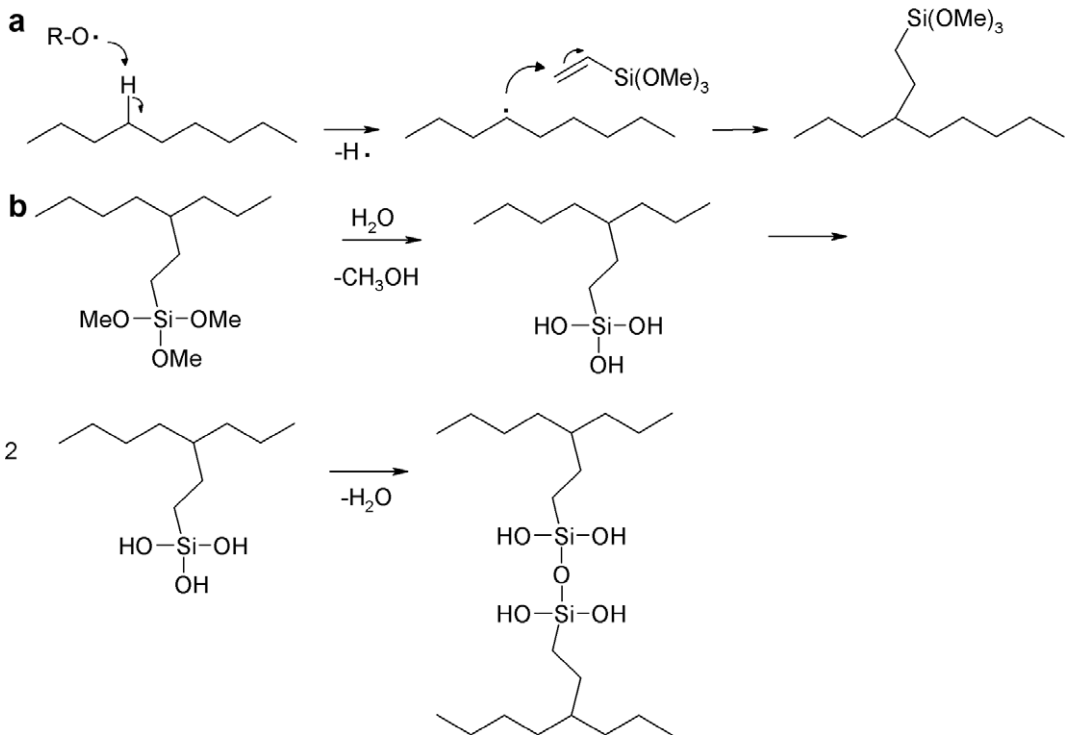

Fig. 1. (a) The reaction mechanism during peroxide induced melt grafting of vinyl silane onto polyethylene, (b) the hydrolysis step and condensation step during the silane cross-linking reaction.

components as well [11]. Phenoxyl free radicals in lignin can react with oxygen and/or with functional groups in the cell wall to form quinones, the coloured chromophores [11]. Muasher and Sain [9] proposed that two competing reactions were responsible for colour fading and changes in yellowing of WPC upon weathering. The first reaction was oxidation of lignin to paraquinone chromophoric structures which was dominant during the first 250 h of UV-exposure. The second was reduction of the paraquinone structures to hydroquinones which leads to photobleaching. Stark [10] also showed that the colour fading of WPC was more severe during exposure to xenon arc radiation and water spray simultaneously than when the composites were exposed to only xenon arc radiation. This was explained as a result of a combination of different possible effects, such as removal of extractives during water spraying, an acceleration of the oxidation reactions in wood as a result of the presence of water, and swelling of the wood fibre cell wall which facilitated light penetration into the wood.

The mechanical properties of WPC have shown to deteriorate during accelerated weathering studies [6–8,10]. The loss in mechanical properties upon accelerated weathering has been reported to be mainly due to the effect of absorbed moisture [8,10]. However, photodegradation at the polyethylene–wood interface will contribute to the loss in mechanical properties upon weathering [8,10]. Moisture has been reported to degrade the interface and thus decrease the strength as a result of less efficient stress transfer between the wood fibre and the polymer–matrix [10]. Moisture will also swell the wood fibre cell wall which can cause interfacial cracks and thus a decrease in the modulus of the composites [10]. In addition, formation of cracks in the matrix will enhance water penetration into the composites which lead to further loss in the mechanical properties [7,10]. Water absorption–freeze–thaw cycling of WPC has also shown to result in a significant loss in the flexural properties [12,13]. During cycling the composite developed cracks and the interface between the wood fibre and the polymer–matrix degraded in the composites. This was believed to be caused by the effect of moisture during the cycling of the composites.

In our previous studies, we have shown that the problems with toughness and long-term loading of WPC can be improved by the use of silane cross-linking technology [14–17]. Silane cross-linking improved the toughness and impact strength of the composites through improved bonding at the wood–matrix interface. In addition, the creep deformation during long-term loading showed a decreasing trend due to a combination of the silane cross-linked polyethylene matrix and improved interfacial adhesion. Silane cross-linked polyethylenes are a commercial product for the global wire and cable market. The silane cross-linking technique does not suffer from high investment cost and the ethylene-vinyl silane copolymer can be processed and shaped in conventional thermoplastic processing equipment and subsequently cross-linked after processing [18]. Vinyl silanes can be grafted onto the polyethylene backbone by reactive extrusion. The grafting reaction is usually initiated by the use of small amounts of peroxide. The per-

oxide decomposes when heat-treated and form oxyradicals which can abstract hydrogen from the polyethylene chains and convert it into macroradicals, see Fig. 1a [19,20]. These macroradicals can then attack the vinyl group on the vinyl silanes and chemically bond it onto the polyethylene backbone. The cross-linking reaction between grafted silane groups is then initiated by trace amounts of water and proceeds over two steps, see Fig. 1b [19,21]. In the first step the methoxyl groups are hydrolysed to hydroxyl groups and methanol is removed. The cross-linking takes place in the second step where the hydroxyl groups recombine through a condensation step.

This study has been focused on manufacturing of silane cross-linked composites and evaluation of the durability and mechanical properties of the composites. Silane cross-linkable composites were produced by reactive extrusion and thereafter manufactured into rectangular profiles. The composites were cured in a hot and humid sauna to increase the degree of cross-linking in the composites. These cross-linked composites were evaluated regarding their durability and mechanical properties in comparison with two non-cross-linked wood fibre–polyethylene composite systems.

2. Experimental

2.1. Materials

High density polyethylene, Exxon Mobile Chemicals HD6733 (MFI = 33 g/10 min, 190 °C/2.16 kg) and Petrothene LM 6007-00 (MFI = 0.8 g/10 min, 190 °C/2.16 kg), were purchased from Channel Prime Alliance (Norwalk, CT, US) and Lyondell Chemical Company (Houston, TX, US), respectively. Pine wood flour (40 mesh) was provided from American Wood Fiber (Schofield, WI, US). Vinyltrimethoxy silane 98% and dicumyl peroxide 99% were purchased from Sigma–Aldrich (Leirdal, Norway). Lubricant, Struktol TMW113 was purchased from Struktol Company of America (Stow, OH, US). In this study, three different composite formulations were prepared, a cross-linked composite and two non-cross-linked formulations. The non-cross-linked composites are referred to as ''High-MFI'' and ''Low-MFI'', respectively, corresponding to the melt flow index of the polyethylene matrix in the composites.

2.2. Processing

The wood flour was dried for 24 h at 105 °C to a moisture content of ~0.9% (based on dry weight) before the compounding process. Plastic granulates and wood flour were compounded using a 32 mm Davis-Standard (Pawcatuck, CT, USA) co-rotating twin-screw extruder with seven temperature zones. The plastic and the wood flour were fed to the extruder at temperature zone 1 with Schenk AccuRate (Whitewater, WI, USA) gravimetric feeders. The zone temperatures ranged between 171 and 193 °C, the screw speed was 200 rpm, the melt pressure at the die varied between 15 and 39 bar depending on material blend, and the material output was 6.8 kg/h. Silane cross-linked composites were produced by pumping a solution of vinyltrimethoxy silane and dicumyl peroxide (12:1 w/w) into the extruder at temperature zone 1. The amount of added silane solution to the composites was 2% w/w. Vacuum venting at temperature zone 8 was used to minimize volatile extractives and un-reacted silane in the final samples. The extruded composite strands were cooled with compressed air and pelletized using a Primo 120E (Rieter, Spartanburg, SC, USA) pelletizer. The composite formulations are shown in Table 1.

The compounded composite pellets were dried for 24 h at 105 °C to a moisture content of ~0.3% (based on dry weight) before the profiling. Profiles were produced in the same co-rotating extruder through a rectangular die measuring 6.4 × 60 mm. The composite pellets (96% w/w) and lubricant (4% w/w) were gravimetrically fed to the extruder at temperature zone 1. The temperatures were between 191 and 116 °C, the screw speed between 150 and 30 rpm, the melt pressure at the die varied between 0 and 17 bar, and the material output was 6.8 kg/h. A water spray tank was used to cool the extruded profiles and a puller pulled the profiles at a constant speed through the water spray tank. Standard flexural test specimens for mechanical testing were cut from the profiles (3.2 × 12.7 × 127 mm). Some of the silane cross-linkable composites were cured at room temperature and others were cured for 48 h in a simulated sauna. The curing conditions in the humid sauna were close to saturation and the temperature was 90 °C. The sauna cured composites were subsequently dried to their initial weight before testing.

2.3. Gel content

The gel content of the composites was determined using *p*-xylene extraction according to ASTM D2765 [22]. The specimens to be analysed were ground and placed in folded 120 mesh stainless steel cloth cages. Cages with ground samples were weighed before immersion in the *p*-xylene. Butylated hydroxytoluene (BHT) was used as an antioxidant to inhibit further cross-linking of the specimen and 1% of BHT was dissolved in the *p*-xylene. The cages with ground material were then extracted in boiling *p*-xylene/BHT solution (143 °C) for 12 h. Extracted specimens were then dried at 150 °C until a constant weight was attained and subsequently re-weighed. The gel content of the differ-

Table 1
Composite formulations

Sample code	Weight%			
	HDPE	HDPE	Wood flour	Silane solution
	MFI = 33	MFI = 0.8		
High-MFI	60	–	40	–
Low-MFI	–	60	40	–
Cross-linked	58	–	40	2

ent blends was determined as the average of three separate replicates. The gel-content was calculated according to the following equation:

$$\text{Extract } \% = (\text{weight lost during extraction})/(\text{weight of original specimen} - \text{weight of wood})$$

$$\text{Gel content} = 100 - \text{Extract } \% \quad (1)$$

2.4. Mechanical testing

Flexural properties of the composites were measured on a Tinius Olsen H5K-S UTM materials testing machine (Horsham, PA, US) in accordance with ASTM D790 [23]. The dimensions of the specimens tested were approximately $3.2 \times 12.7 \times 127$ mm. The measurements were performed at ambient conditions, i.e. a temperature of 23 °C and a relative humidity of approximately 50%. At least 10 specimens of each blend were tested.

Short-term creep experiments of composites were performed using a Rheometrics Dynamic Mechanical Thermal Analyzer DMTA V (Rheometric Scientific, Piscataway, NJ, USA). The measurements were performed in dual cantilever mode on specimens measuring approximately $2 \times 12 \times 30$ mm. The creep response of the composites was measured when subjected to an applied static stress of 3 MPa for 3 days and subsequently 3 days of recovery. All experiments were performed at a temperature of 30 °C.

2.5. Boiling test

A boiling test was performed by immersing composites in boiling water for 3 h. Rectangular composite specimens measuring approximately $3.2 \times 12.7 \times 35$ mm was used in the test. The specimens to be analysed were first conditioned at 23 °C and 50% relative humidity for 48 h and subsequently weighed before immersion in the boiling water. After boiling the surface water was removed and the specimens weighed again. The moisture absorption of the composites during the boiling test could thus be determined gravimetrically. Moisture absorption was determined for three replicates of each blend, and the average is reported.

2.6. Durability

The composite samples were placed in a xenon arc-type accelerated weathering testing equipment and were exposed to light radiation with water spray according to ASTM D2565 [24]. The light radiation was filtered with borosilicate filters resulting in a radiation source similar to solar radiation, i.e., consisting of ultraviolet, visible, and infrared radiation. Samples were mounted on a drum that rotated around the xenon arc bulb at 1 rpm. The 2 h water spray cycle consisted of 108 min of light exposure and 12 min of simultaneous water spray and light exposure. An irradiance sensor was used to measure light intensity for wavelengths from 300 to 400 nm (XenoCal, Atlas Materials Testing Technology, Linsengericht, Germany). The radiant energy (time integral of irradiance) was calculated. The composites were removed after 1000, 2000, and 3000 h, which corresponded with a radiant energy exposure of 31, 62, and 93 J/m^2, respectively. After each weathering period the composites were measured for surface colour characteristics and mechanical properties.

Water absorption–freeze–thaw (WFT) cycling of the composites was performed in accordance with ASTM D6662-01 [25]. The cycling consisted of three steps: (1) water soaking in a water bath at 21 °C until the samples reached equilibrium moisture content, (2) freezing for 24 h in a freezer (Siemens, Siemens-Elektrogeräte, Germany) at −27 °C, (3) thawing at 23 °C and approximately 50% RH for 24 h. All composites were exposed to five WFT cycles. Ten replicates of each blend were mechanically tested after five WFT cycles.

2.7. Colour measurements

The surface colour of weathered and un-weathered composites was measured with a Minolta CR-200 Chroma Meter (Minolta Corp., Ramsey, NJ). The CIELAB colour system was used to measure the surface colour in L^*, a^*, b^* coordinates. L^* represents the lightness coordinate and varies from 100 (white) to 0 (dark), a^* represents the red ($+a^*$) to green ($-a^*$) coordinate, and b^* represents the yellow ($+b^*$) to blue ($-b^*$) coordinate. The colour difference was calculated as outlined in ASTM D2244 according to the following equation [26]:

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

where ΔL^*, Δa^*, and Δb^* represents the difference between the initial and final values of L^*, a^*, and b^*, respectively. It should be noted that ΔE^* represents the magnitude of the colour difference, but does not indicate the direction of the colour difference. The surface colour for five replicates was measured at two locations on each composite sample.

3. Results and discussion

3.1. Processing

Polyethylene and wood flour were compounded in a co-rotating twin screw extruder. The cross-linked composite was manufactured by reactive compounding during which time the grafting of the vinyltrimethoxy silane and the compounding of the polyethylene and wood flour were carried out simultaneously. This makes the production of the composites more economical and feasible on an industrial scale. Moreover, a one-step process also gives the possibility of grafting silane onto both polyethylene and wood flour.

Addition of the silane solution during reactive compounding increased the motor load (29–43%) and the melt pressure (15–39 bar) compared to compounding of the non-cross-linked high-MFI composite. This is caused by an increase in melt viscosity as a result of premature cross-linking but as also is a result of interaction between grafted silane groups [27]. The motor load and melt pressure were equally high (43% and 44 bar) during compounding of the low-MFI composite due to its high melt viscosity. Compressed air was used to cool the extruded strands before granulation. Air was used instead of water to prevent premature cross-linking before the profiling step.

The compounded granulates were profiled into rectangular profiles with a cross-section of approximately 6.4×60 mm. The cross-linked composite and the low-MFI composite were easier to handle downstream due to the higher melt viscosity than the high-MFI composite. The melt temperature was lowered until the profiles achieved a regular and smooth structure. It was not possible to achieve a completely smooth surface structure of the high-MFI profile due to the low melt viscosity.

3.2. Degree of cross-linking

The degree of cross-linking in the composites was determined by gel content measurements. Cross-linked polyethylene is insoluble in boiling *p*-xylene while the non-cross-linked part is soluble. The gel content thus corresponds to the cross-linked part of the polyethylene and is determined by calculating the weight loss during *p*-xylene extraction. The results from the gel content measurements are summarised in Table 2. As shown in the table, no gel was formed in the composites where no silane solution was added. The average gel content in the silane cross-linked composite cured at room temperature (RT) was 33%. A previous study showed that curing of silane cross-linkable composites at room temperature did not significantly affect the gel content in the composites [15]. The degree of cross-linking in the composites cured at room temperature is thus believed to correspond to the cross-linking that took place during the processing. Curing the silane cross-linked composites in a humid sauna at 90 °C near saturation increased the average gel content to 59%. The silane cross-linking reaction is initiated by moisture. Curing the composites in a humid environment at elevated temperature thus increased the degree of cross-linking in the composites. Previous studies have shown that the maximum gel content of silane cross-linked polyethylene is in the range between 70% and 80% [16,21]. It was shown that an addition of 4% w/w or more of the silane solution during processing was necessary to fully cross-link the composites cured at 90 °C near saturation, when no catalyst was used [16]. The addition of silane solution in this study was limited to 2% w/w since at higher levels of silane solution, the melt pressure limit of the extruder was reached.

The gel content at different depths throughout the profile was also measured to determine if there was any difference in the degree of cross-linking over the thickness. After curing the composite profiles in a humid sauna at 90 °C near saturation for 48 h, gel content measurements were performed at 0–0.5, 0.5–1, 1–2, 2–3 mm from the surface of the profiles. The results from the gel content measurements at different levels into the profiles are summarised in Table 3. The Student's *t* test was used at $p = 0.05$ to identify significant differences in gel content at the various depths. Beyond 0–0.5 mm, there was no significant difference in the gel content through the thickness of the composites. However, the gel content showed to be slightly lower (56%) in the surface layer (0–0.5 mm) of the composites. From 0.5 to 3 mm into the composites the gel content was almost constant at 60%. The reason for the slightly lower degree of cross-linking in the surface layers of the composites can be attributed to an enrichment of polyethylene at the surface as a result of the profiling process. A small deviation of the wood flour content in the surface layers will generate a lower gel content (see Eq. (1)). These results show that sufficient moisture was present at different levels into the composite profiles to achieve equivalent degree of cross-linking through the thickness (6.4 mm).

3.3. Mechanical testing

The flexural properties of the composites were tested in accordance with ASTM D790 [23]. Characteristic stress–strain curves of the composites are shown in Fig. 2. All the results from the mechanical testing are summarised in Table 4. The Student's *t* test was used at $p = 0.05$ to identify significant differences between composite formulations for a specific property. In Table 4, significant property differences between composite formulations are denoted by different superscripts. The flexural modulus was significantly higher for the low-MFI and the cross-linked composites than the high-MFI composites. This indicates that

Table 2
Gel content of the composites

Sample code	Gel content (%)
High-MFI	0
Low-MFI	0
Cross-linked-RT	32.9 ± 0.5
Cross-linked-Sauna	59.4 ± 1.1

Table 3
Gel content at different depths in the cross-linked composite profiles

Distance from surface (mm)	Gel content (%)
0–0.5	56.2 ± 0.4^{A}
0.5–1	60.0 ± 1.5^{B}
1–2	58.1 ± 0.7^{B}
2–3	58.8 ± 1.2^{B}

Averages and standard deviations are reported. The superscripts denote significant differences between values.

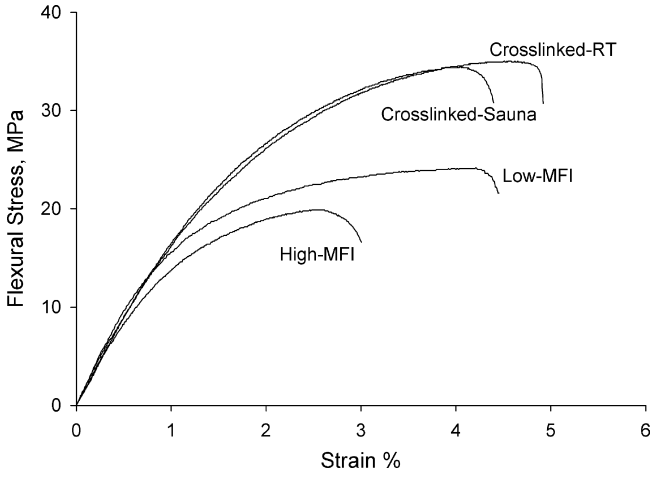

Fig. 2. Characteristic stress–strain curves of the composites.

both switching to a lower MFI HDPE and cross-linking the HDPE can result in improvements in flexural modulus. This is believed to be caused by an increase in stiffness of the polyethylene matrix with an increase in molecular weight.

Both the low-MFI composites and the cross-linked composites showed significantly improved flexural strength compared with the high-MFI composites. The cross-linked composites also showed a further significant increase in flexural strength compared with the low-MFI composites. Improved adhesion between the wood and the polyethylene matrix is most likely the reason for the significant improvement in flexural strength of the cross-linked composites. The improved adhesion could be due to covalent bonding between wood and silane grafted polyethylene through either condensation or free-radical reaction. Moreover, hydrogen bonding between silanol groups grafted on polyethylene and hydroxyl groups on wood, as well as van-der-Waals forces between condensated silane on wood and the polyethylene matrix, can improve the adhesion between the phases. Curing the cross-linked composites in a high humidity sauna increased the degree of cross-linking significantly from 33% to 59% in the tested composite samples. Even so, the flexural strength of the composites cured in a sauna did not differ significantly from the cross-linked composites stored at room temperature. This indicates that the reactions responsible for improving the adhesion between wood and polyethylene mainly takes place during the higher processing temperature. The reason for the higher flexural strength of the low-MFI composite than the high-MFI composite is probably due to higher strength of the high molecular weight polyethylene matrix in the low-MFI composite. As can be seen in Fig. 2, and is reported in Table 4, the elongation at break of the cross-linked and low-MFI composites were also significantly higher than for the high-MFI composite. The improvement in elongation at break of the composites can be due to improved matrix properties but also due to improved adhesion between the matrix and the wood fibre in the cross-linked composites.

Short-term creep experiments were performed using a dynamic mechanical thermal analyzer, DMTA V. The experiments were performed to study the effect of silane cross-linking on the creep properties of the composites. Fig. 3 shows the results from the creep experiment showing strain as a function of time on logarithmic scales. The creep response after 3 days of loading was significantly lower in the cross-linked composite (cured in a sauna) than in the non-cross-linked composites (high-MFI and low-MFI). The average creep rate during loading for the high MFI, the low-MFI, and the cross-linked composites cured in a sauna was 77, 80, and 39 μm/day, respectively. It is interesting to note that the average creep rate during loading was twice as fast for the non-cross-linked composites as for the cross-linked composite. The creep response of the low-MFI composite was lower than for the high-MFI com-

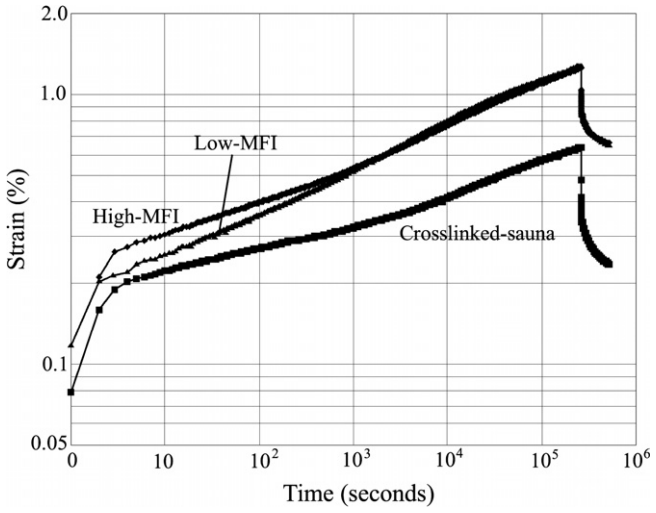

Fig. 3. Strain as a function of time during creep experiments at 30 °C. A constant stress of 3 MPa was applied during the loading time.

Table 4
Mechanical properties of the composites

Sample code	Modulus (GPa)	Strength (MPa)	Elongation at break (%)
High-MFI	1.6 ± 0.2^{A}	19.4 ± 2.3^{A}	2.8 ± 0.7^{A}
Low-MFI	2.0 ± 0.3^{B}	24.0 ± 1.1^{B}	4.2 ± 0.3^{B}
Cross-linked-RT	1.9 ± 0.3^{B}	36.2 ± 3.0^{C}	4.5 ± 0.2^{C}
Cross-linked-Sauna	1.9 ± 0.2^{B}	33.9 ± 2.2^{C}	3.9 ± 0.2^{D}

Averages and standard deviations are reported. The superscripts denote significant differences between composites for that property.

posite below ~1500 s. However, the creep rate of the low-MFI composite was faster than for the high-MFI composite and the creep curves crosses each other at about 1500 s (~25 min). The creep rate of the two composites was thereafter quite similar. After 3 days of recovery the non-recoverable deformation was also larger in the non-cross-linked composites (~0.7%) than in the cross-linked composite (~0.2%). The improved creep properties of the cross-linked composite are believed to be related to a reduced viscous flow of the polyethylene matrix due to cross-linking as well as improved adhesion between the polyethylene matrix and the wood fibres. In an earlier study of silane cross-linked composites, it was also shown that a higher degree of cross-linking lowered the creep response [16].

3.4. Boiling test

The moisture absorption after 3 h in boiling water was used as an indirect measurement of the interfacial adhesion between the polyethylene matrix and the wood fibres of the composites. In case of good adhesion the moisture absorption of the composites would not be as significant as if adhesion is lacking. A higher moisture content is thus an indication of poor encapsulation of the wood flour by the polymer–matrix which acts as a barrier to water penetration to the system. The average moisture absorption of the composites after boiling is presented in Table 5. The cross-linked composites absorbed considerable less moisture (1.7%) during the boiling than did the high-MFI composites (3.7%) and the low-MFI composites (3.0%). The improved water resistance of the cross-linked composites is most likely related to a better bonding between the wood fibres and the polymer–matrix.

3.5. Durability

Accelerated weathering of the composites was performed in accordance with ASTM D2565 [24]. The composites were exposed to xenon arc radiation with water spray for different periods of time to study the effect of weathering on the mechanical properties and surface colour of the composites. The mechanical properties after weathering was very similar for the cross-linked composites cured at room temperature and in the high humidity sauna. Therefore, only the results for the cross-linked composites cured at room temperature are shown here. Figs. 4 and 5 show the flexural modulus and strength, respectively, after 1000, 2000, and 3000 h of weathering relative to un-weathered composites. The standard deviations in the figures were normalized in the same way. As can be seen in the figure it is hard to make conclusive statements about the modulus and strength of the composites since the standard deviations overlap each other. The trend, however, is that the mechanical properties of the composites deteriorate with increased weathering time. Statistically with a 95% confidence level there was a decrease in both the modulus and strength of all of the composites after 3000 h of weathering. Moisture absorption of the hydrophilic wood fibre is believed to be the main reason for the loss in the mechanical properties of the composites upon weathering. Earlier studies have shown that although photodegradation of the polyethylene/wood can explain some of the loss in mechanical properties upon weathering the main reason for the mechanical property loss is the water absorption [8,10]. Absorption of moisture will soften the composites and it has been reported that swelling of the wood fibre cell

Table 5
Moisture absorption of the composites after 3 h in boiling water

Sample code	Moisture absorption (%)
High-MFI	3.7 ± 0.2
Low-MFI	3.0 ± 0.3
Cross-linked-Sauna	1.7 ± 0.1

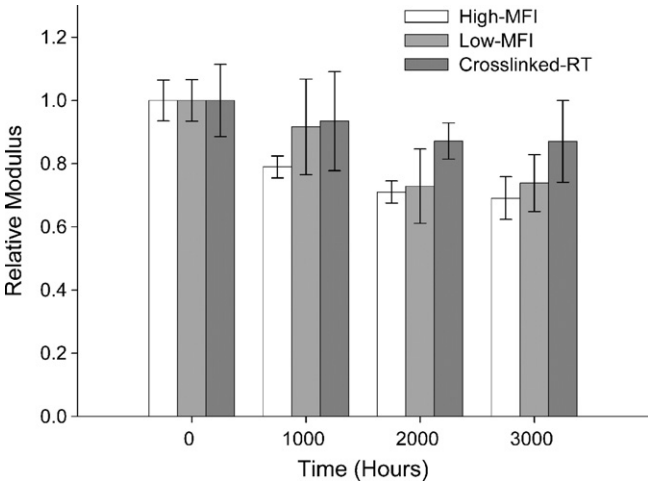

Fig. 4. The flexural modulus of the composites after 1000, 2000, and 3000 h of accelerated weathering relative un-weathered composites. The standard deviations are also normalized values.

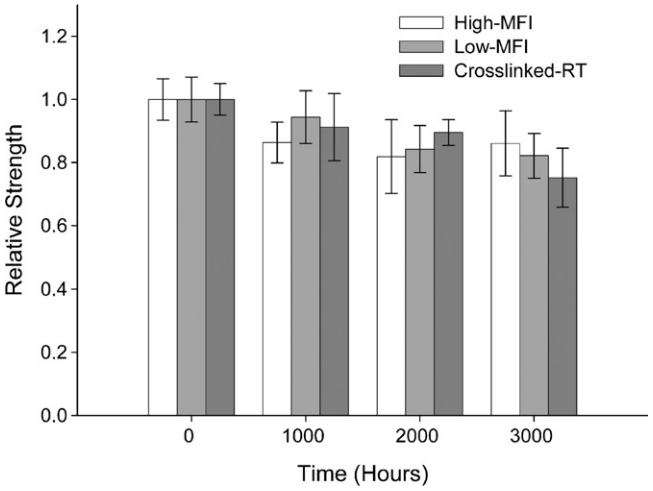

Fig. 5. The flexural strength of the composites after 1000, 2000, and 3000 h of accelerated weathering relative un-weathered composites. The standard deviations are also normalized values.

wall as a result of moisture absorption can cause cracks in the matrix which lower the modulus [10]. The decrease in modulus after weathering seems less for the cross-linked composites than for the non-cross-linked composites. This is believed to be due to a better adhesion between the wood and polyethylene phases in the cross-linked composites which improve the moisture resistance.

After 3000 h of weathering the loss in flexural strength appeared largest for the cross-linked composites. This can be due to the effect of moisture and UV-light that degrades the interfacial quality in the cross-linked composites. The adhesion between the wood and polyethylene phases was better for the cross-linked composites compared with the non-cross-linked composites. It is likely that the covalent bondings (proposed in the mechanical testing section) between the wood and the silane grafted polyethylene can be attacked during UV-light exposure. In addition, moisture can replace secondary interactions such as hydrogen bonding between grafted silanol groups on polyethylene and hydroxyl groups on the wood fibres. Since the adhesion between the wood and polyethylene phases was already rather low in the non-cross-linked composites, the decrease in strength after weathering was not as great as for the cross-linked composites. However, the average strength of the cross-linked composites after 3000 h of weathering was still 55% higher than the high-MFI composite and 24% higher than the low-MFI composite.

The surface colour of un-weathered and weathered composites was measured in accordance with ASTM D2244 [26]. Fig. 6 shows the difference in surface colour between un-weathered and weathered (3000 h) composites. As can be seen in the figure, there was a significant colour fading at the surface for all of the composites upon weathering. This is in agreements with previous studies on weathering of unstabilized WPC with a high density polyethylene matrix [6,7,9,10]. Photodegradation of the wood components (mainly lignin) has been reported to be the main reason for the colour fading although the polymer–matrix also have shown to contribute to the colour fading but to a smaller extent [6,7,9]. Because more fading occurs when WPCs are exposed to light radiation with water spray than exposure to only light radiation, it has also been postulated that fading is partly the result of the removal of water soluble, colour imparting extractives in the wood [10]. The difference in surface lightness ($L^*_{\text{weathered}}$–$L^*_{\text{un-weathered}}$) of the composites as a function of weathering time is presented in Fig. 7. The standard deviations in the figure were calculated according to the following equation $\sigma = \sqrt{\sigma^2_{L^*_{\text{weathered}}} + \sigma^2_{L^*_{\text{un-weathered}}}}$. All of the composites increased their surface lightness with prolonged time in the weathering chamber. The increase in lightness was more pronounced during the first 1000 h of weathering and then levelled off between 2000 and 3000 h. After 3000 h of weathering the increase in lightness seemed largest for the cross-linked composites (79%) followed by the low-MFI composites (61%) and the high-MFI composites (52%). However, it should be noted there was an overlap in the standard deviations for the lightness difference between the cross-linked and the low-MFI composites and between the low-MFI and the high-MFI composites. Although the increase in lightness upon weathering was largest for the cross-linked composites the final lightness value was lowest for those composites. This was due to the fact that the cross-linked composites were slightly darker than the high-MFI and the low-MFI composites before weathering, as shown in Fig. 6. The total colour change (ΔE^*) at the surface of the composites as a function of weathering time is shown in Fig. 8. As can be seen in the figure, the total colour change was also more pronounced for the cross-linked composites than for the low-MFI and high-MFI composites.

All the data from the colour measurements are summarised in Table 6. The total colour change at the surface of

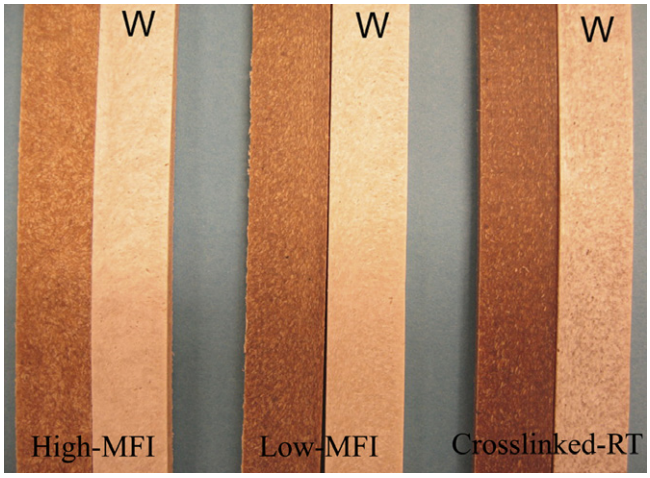

Fig. 6. The difference in surface colour between un-weathered and weathered (3000 h) composites. The weathered composites are denoted with a "W".

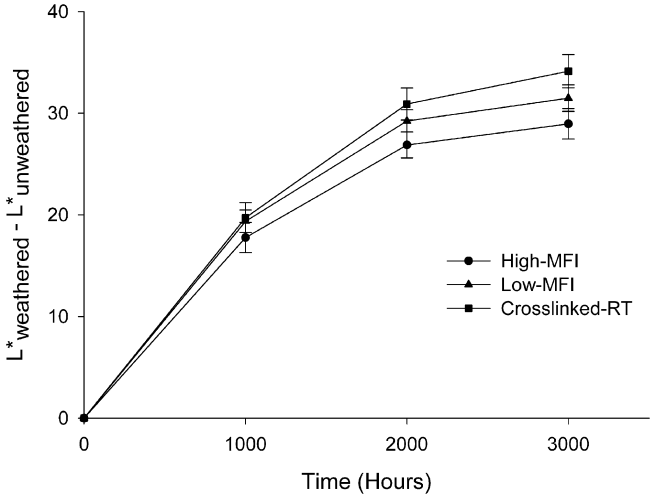

Fig. 7. The difference in surface lightness ($L^*_{\text{weathered}}$–$L^*_{\text{un-weathered}}$) of the composites as a function of weathering time. The standard deviations were calculated according to the following equation $\sigma = \sqrt{\sigma^2_{L^*_{\text{weathered}}} + \sigma^2_{L^*_{\text{un-weathered}}}}$.

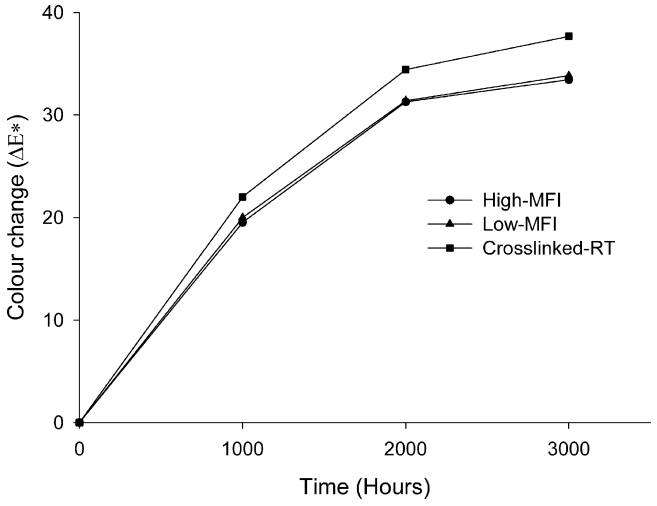

Fig. 8. The total colour change (ΔE) of the composites as a function of weathering time.

Table 6
Colour parameters of the composites after 0, 1000, 2000, and 3000 h of accelerated weathering

Colour parameters	Weathering time (h)	High-MFI	Low-MFI	Cross-linked-RT
L^*	0	55.5 ± 1.1	51.2 ± 0.8	43.5 ± 0.6
L^*	1000	73.3 ± 1.0	70.6 ± 0.8	63.2 ± 1.3
L^*	2000	82.4 ± 0.7	80.5 ± 0.8	74.4 ± 1.5
L^*	3000	84.4 ± 1.1	82.7 ± 1.1	77.6 ± 1.5
a^*	0	8.0 ± 0.4	6.9 ± 0.2	9.0 ± 0.3
a^*	1000	5.1 ± 0.4	4.8 ± 0.2	4.2 ± 0.2
a^*	2000	2.0 ± 0.2	2.2 ± 0.1	2.1 ± 0.2
a^*	3000	1.7 ± 0.3	1.8 ± 0.2	1.7 ± 0.3
b^*	0	19.6 ± 0.8	16.5 ± 0.8	16.8 ± 0.5
b^*	1000	12.0 ± 1.2	11.9 ± 0.6	8.3 ± 0.5
b^*	2000	4.8 ± 0.6	6.0 ± 0.4	3.3 ± 0.4
b^*	3000	4.1 ± 0.7	5.1 ± 0.7	2.7 ± 0.4

the high-MFI and low-MFI composite after 3000 h of weathering was very similar. The colour of the composites decreased in red intensity (a decrease in a^*) and yellow intensity (a decrease in b^*). This indicates that in addition to colour fade (a decrease in L^*), the composite is becoming more white. The more pronounced colour change of the cross-linked composites was mainly caused by a larger increase in lightness and a larger shift away from red upon weathering. A possible explanation for the more significant colour change at the surface of the cross-linked composites could be related to a larger amount of free radicals in these composites. A small amount of peroxide was used to initiate the free radical reaction upon which the vinyl silane was grafted onto polyethylene or wood. The free radical reaction will most probably leave some un-reacted polyethylene or wood macroradicals in the cross-linked composites. These free radicals will probably accelerate the photodegradation of the composites and can thus explain the larger colour change of these composites.

Water absorption–freeze–thaw (WFT) cycling of the composites was performed in accordance with ASTM D6662 [25]. This was carried out to study if cross-linking could be a way to improve the loss in mechanical properties that has been reported during WFT-cycling of WPC [12,13]. According to the standard the WPC should be subjected to at least three WFT-cycles. In this study, the composites were subjected to five WFT-cycles and thereafter tested for its flexural properties according to ASTM D790. A visual characterisation after five WFT-cycles showed only minor fading of the composites compared to un-cycled composites. This was expected since the composites were not subjected to any UV-light during the experiment. Figs. 9 and 10 show the flexural modulus and strength, respectively, after five WFT-cycles relative to the un-cycled composites. The standard deviations in the figures were normalized in the same way. The mechanical properties after WFT-cycling were very similar for the cross-linked composites cured at room temperature and in the high humidity sauna. Therefore, only the results from the cross-linked composites cured at room temperature are shown here. As can be seen in Fig. 9, there was no significant decrease in modulus (5% decrease) for the cross-linked composites after the WFT-cycling when taking the standard deviations into account. At a 95% confidence level there was no statistically significant decrease in modulus for the cross-linked composites after WFT-cycling. The modulus of the non-cross-linked composites, on the other hand, decreased significantly after WFT-cycling with a 18% decrease for the high-MFI composites and a 26% decrease for the low-MFI composites. This is again believed to be explained by the better moisture resistance of the cross-linked composites due to a better adhesion between the polyethylene and wood fibres. After five WFT-cycles, the non-cross-linked composites absorbed almost twice the amount of moisture compared to the cross-linked composites. The absorbed moisture content

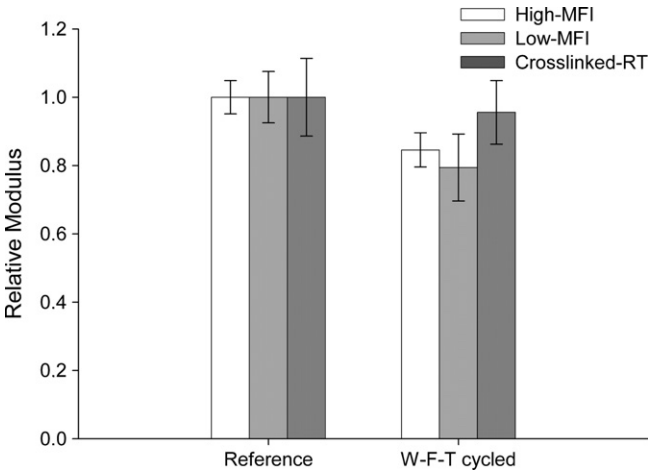

Fig. 9. The flexural modulus of the composites after five water absorption–freeze–thaw (WFT) cycles relative un-cycled composites. The standard deviations are also normalized values.

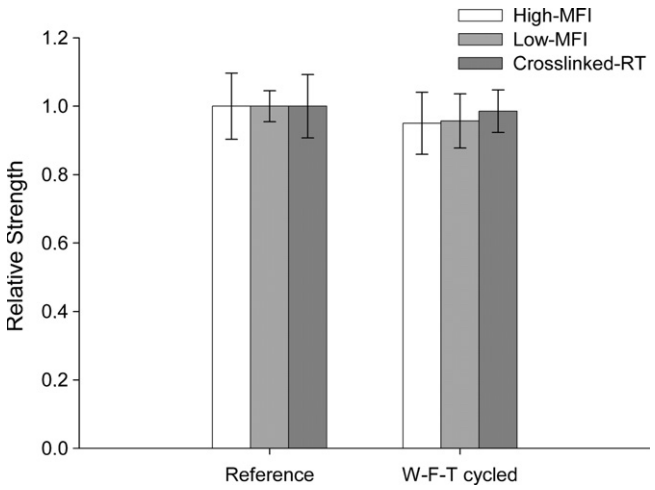

Fig. 10. The flexural strength of the composites after five water absorption–freeze–thaw (WFT) cycles relative un-cycled composites. The standard deviations are also normalized values.

after cycling was 1.4%, 1.3%, and 0.7% for the high-MFI, low-MFI, and cross-linked-RT composites, respectively. This confirms the better moisture resistance property of the cross-linked composites. Previous studies have also reported that the effect of moisture during WFT cycling is the main reason for the loss in the mechanical properties of the composites [12,13]. In those studies, it was shown that absorbed moisture caused cracks in the composites and degraded the interfacial quality upon the cycling. In Fig. 10, the relative strength of the composites after five WFT cycles is presented. Taking the standard deviation into account there was no significant decrease in strength after the cycling for any of the composites. At a 95% confidence level there was no statistic decrease in strength for the composites. Pilarski and Matuana [13] showed a loss of about 5% in strength and near 38% in stiffness for high density polyethylene/pine wood flour composites (50 weight% wood) after 15 WFT cycles.

4. Conclusions

Silane cross-linked wood–polyethylene composite profiles were manufactured by reactive extrusion. Addition of silane solution (2% w/w) during compounding increased the melt viscosity significantly as a result of both premature cross-linking and interaction between grafted silane groups. The cross-linking reaction was shown to be initiated already during the extrusion process. Curing the composites in a sauna at elevated temperature near saturation increased the degree of cross-linking from approximately 30% to 60%. The gel content showed to be slightly lower (56%) in the surface layer (0–0.5 mm) of the composites. However, beyond the surface layer there was no significant difference in the gel content through the thickness of the composites.

The silane cross-linked composites showed flexural toughness superior to the non-cross-linked composites. An addition of only 2% w/w of silane solution during processing improved the flexural strength with almost 90% compared to the high-MFI composite and about 50% compared to the low-MFI composite. Improved adhesion between the wood fibre and the polyethylene matrix is most likely the reason for the significant improvement in toughness of the cross-linked composites. The cross-linked composites also absorbed less moisture during a boiling test in water and this was an indirect evidence of improved interfacial adhesion. The flexural modulus was significantly higher for the low-MFI and the cross-linked composites than the high-MFI composites. Cross-linking also showed to be an efficient way to improve the creep properties of the composites. The creep rate during loading was lowered by 50% and the non-recoverable deformation after recovering was decreased from 0.7% in the non-cross-linked composites to 0.2% in the cross-linked composites.

It was hard to make certain statements of the modulus and strength of the composites after accelerated weathering for 1000–3000 h since the standard deviations was overlapped. However, the trend was a decrease in both flexural modulus and strength upon weathering. Moisture absorption of the hydrophilic wood fibres is believed to be the main reason for the loss in the mechanical properties of the composites upon weathering. It is also likely that the ultraviolet radiation attacked the bond between the wood and the cross-linked HDPE matrix, further degrading the interface. The relative decrease in modulus seemed to be lower for the cross-linked composites while the decrease in strength seemed to be higher compared to the non-cross-linked composites. On the other hand, the strength of the cross-linked composites after 3000 h of weathering was still 55% higher than the high-MFI composite and 24% higher than the low-MFI composite. All the composites experienced a considerable colour fading upon weathering. The colour change was more pronounced for the cross-linked composites and was believed to be related to a larger amount of free radicals in these composites that accelerate the photodegradation reactions.

Water absorption–freeze–thaw cycling decreased the flexural modulus of non-cross-linked composites considerably while there was no statistical decrease in modulus for the cross-linked composites. The moisture absorption upon cycling was lower in the cross-linked composites and can thus explain the improved durability. There was only an insignificant decrease in strength for the composites after the water absorption–freeze–thaw cycling.

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