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Silane Crosslinked Wood-Thermoplastic Composites

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Abstract

Wood-thermoplastic composites are a more environmental friendly alternative for pressure-treated lumber but can also replace engineering plastic products. These composites have been on the market for more than ten years now and have mainly been used in building and automotive applications. The use of these materials has shown that long-term properties, durability, and toughness are the main problems. The aim of this study was to investigate if silane crosslinking could be one way of solving these problems. Silane crosslinked wood-thermoplastic composites with polyethylene as the matrix and wood flour as reinforcement were manufactured by melt compounding. A reactive extrusion process was developed where compounding of polyethylene and wood flour and silane grafting were carried out simultaneously. The extrusion process was optimized and used in larger scale profiling of crosslinked composites. The composite materials were evaluated using chemical analysis, mechanical testing, spectroscopic analysis, thermal analysis, and electron microscopy. The crosslinking reaction was shown to be initiated during compounding of the composites and was significantly increased upon storage in a high humidity sauna at elevated temperature. The crosslinked composites showed toughness, impact strength and creep properties superior to the non-crosslinked composites. Scanning electron microscopy on the fracture surface of the crosslinked composites revealed good interfacial adhesion between the wood fibres and the polyethylene matrix. Based on results from this study, it is proposed that silane crosslinking creates a three dimensional network in the polyethylene matrix with chemical bonding to the wood fibres.

Future evaluation of results from accelerated weathering studies will reveal if silane crosslinking can improve the durability of wood-thermoplastic composites during outdoor exposure. Investigation of the potential of silane crosslinking on other type of composite systems with other thermoplastic matrices and natural fibres would also be of interest.

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List of Papers

This dissertation is based on work reported in the following papers, referred to by roman numerals in the text.

I. Magnus Bengtsson, Paul Gatenholm, and Kristiina Oksman. The effect of crosslinking on the properties of polyethylene/wood flour composites. Composite Science and Technology 2005; 65(10): 1468-1479.

II. Magnus Bengtsson and Kristiina Oksman. The use of silane technology in crosslinking polyethylene/wood flour composites. In press: Composites Part A.

III. Magnus Bengtsson and Kristiina Oksman. Silane crosslinked wood plastic composites; Processing and properties. Submitted for publication in Composites Science and Technology.

IV. Magnus Bengtsson and Kristiina Oksman. Optimization of silane crosslinking technology for use in polyethylene/wood flour composites. 8th International Conference on Woodfiber-Plastic Composites, Madison, WI, USA, May 23-25, 2005.

V. Magnus Bengtsson, Nicole M. Stark, and Kristiina Oksman. Profile extrusion and mechanical properties of crosslinked wood-thermoplastic composites. Submitted for publication in Polymer Composites.

1. Introduction

1.1 Wood composites

Composite materials are created by combining two or more components to achieve desired properties which could not be obtained with the separate components. Wood composites can be divided in two groups: conventional wood composites and new wood composites. Conventional wood composites such as particle board, fibre board, plywood, oriented strand board, etc., have been on the market for a long time and are well accepted. The wood particles/fibres/veneers in the conventional wood composites are held together with a thermoset adhesive (4-15 weight %)[1]. In the new wood composites, wood fibres are combined with plastics. The difference between the two groups of wood composites is that the polymer content is much higher (~ 50 weight %) in the new wood composites and usually in form of a thermoplastic material. Wood-based composites with a continuous thermoplastic phase provide the opportunity to process the composite using conventional thermoplastic processing equipment[2]. A continuous plastic phase in the new wood composites improves the water resistance and dimensional stability compared to the conventional wood composites where the polymer content is low[3]. The use of a thermoplastic matrix in the new wood composites also makes them recyclable[4].

1.2 Wood-thermoplastic composites

In recent years, the use of wood fibres as reinforcement in plastics has received considerable attention. Wood fibres provide advantages over conventional reinforcing materials in the form of low cost, abundancy, renewability, and low specific gravity[5-7]. In addition, wood fibres also have high specific strength and stiffness[7]. Wood-thermoplastic composites are an alternative material for pressure-treated wood. Pressure treatment of wood with chemical preservatives is necessary to retard biological decay and insect attack[8]. However, the impact these chemicals may have on the environment is cause for concern. In addition, the treatments do little to resist the dimensional changes accompanying moisture absorption[8]. The thermoplastic component in the composites encapsulates the wood and thereby improves the durability against moisture and biological attack[9]. Moreover, wood-thermoplastic composites can be an alternative material for engineering plastic products. Wood-thermoplastic composites can be readily processed in conventional processing equipment for plastics, for example by extrusion and injection moulding. Addition of wood fibres to the thermoplastic matrix increases the stiffness of the material. When proper interfacial adhesion between the wood and the thermoplastic matrix is achieved, the strength of the composite is also higher than for unfilled plastic.

Wood- and natural fibre-thermoplastic composites have successfully penetrated the market in North America. In 2002, the market demand reached 590,000 tons valued at $700 million[10]. This represents a 26 % annual growth since 1998. The major market for wood- and natural fibre-thermoplastic composites in North America is in building products, where approximately two thirds of this total being used in decking and railing applications[10], see Figure 1. Other applications include automotive applications, window profiles, doors, sidings, outdoor/indoor furniture, play courts, flooring etc. Tremendous opportunities and needs for these materials also exist in structural applications for buildings, as well as industrial structures like docks, piers, and bridges[8]. One of the largest manufacturers of wood-thermoplastic decking in North America is Trex Company Inc. (Winchester, VA). Trex decking products are made of recycled plastic grocery bags, reclaimed pallet wrap and waste wood. The material formulation is approximately 50-50 weight % of thermoplastic and wood.

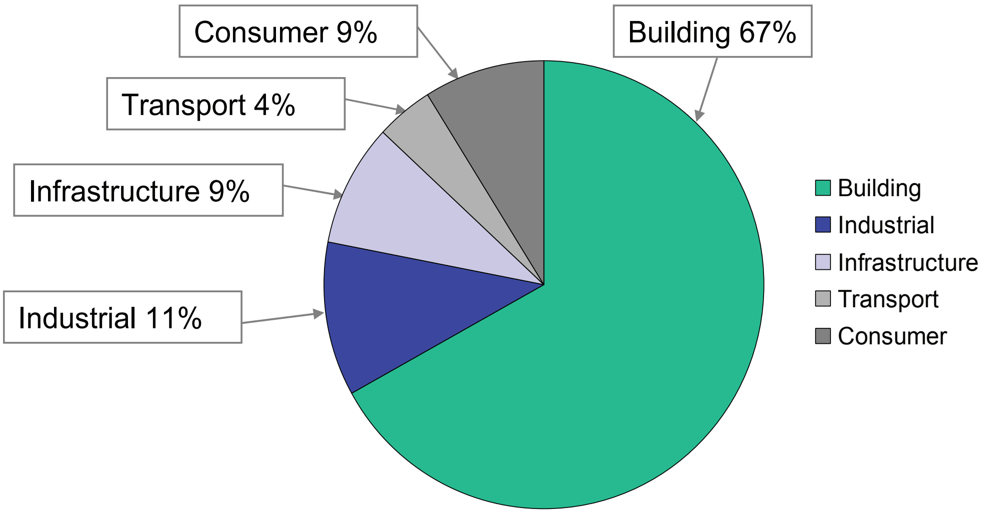

Figure 1. *Application areas for wood- and natural fibre-thermoplastic composites in North America*[10].

In Western Europe, the market for wood- and natural fibre-thermoplastic composites is currently in the early stages of development, totalling $80 million in 2002[10]. In contrast to North America, the European market has been divided into two distinctly separate groups, natural fibre (flax, jute, sisal, hemp, kenaf)-thermoplastic composites and wood-thermoplastic composites. Natural fibre-thermoplastic composites have been widely used in the automotive industry since 1992. Applications for these composites include interior panels, headliners, seat panels, parcel shelves, and acoustic panels[10]. The European wood-thermoplastic composite market is forecasted to grow more quickly from now on. However, the market growth will probably be different from the one in North America since there is no single mass market like decking in Europe.

In spite of all the advantages mentioned above there are also some drawbacks with wood-thermoplastic composites. The main drawback is the low compatibility between the hydrophilic wood and the hydrophobic polymer; this leads to decreased strength and impact properties. Many authors have published work on different types of coupling agents. One of the most commonly used coupling agents is maleic anhydride grafted polyolefins[11-15]. There have also been some studies on other types of coupling agents, such as silanes[16-18], and isocyanates[16-17]. An elastomeric copolymer, maleated styrene-(ethylene-co-butylene)-styrene (SEBS-g-MA), has also been reported to improve both the tensile strength and the impact strength of wood-plastic composites[19]. Moreover, even though the durability of wood-thermoplastic composites during outdoor exposure is superior to that of untreated wood, it is still a problem. With accelerated weathering, wood-thermoplastic composites experience a colour change and loss in mechanical properties[20]. Exposure to ultraviolet (UV) radiation and moisture during outdoor use is of particular concern[20]. Existing wood-thermoplastic composite products are typically used in applications where they are not critical structural elements. Challenges for wood-thermoplastic composites to be utilized in structural applications include lowering product weight and improving the long-term load performance[8]. The density of wood-thermoplastic composites is almost twice that of solid wood[21]. The increase in weight is caused by polymer penetrating into the cell cavity of the wood fibre, thereby increasing the wood fibre density. Foaming is one way of reducing the weight of wood-thermoplastic composites[21-22]. A potential alternative to reducing the weight of the composites is to produce hollow or shaped cross-sections[8]. Thermoplastic materials show a time-dependent behaviour when subjected to constant load. Creep is the increase in deformation over time when a material is subjected to a constant load. Crosslinking of the thermoplastic matrix is one way to reduce the creep during long-term loading of wood-thermoplastic composites[23-24].

1.3 Crosslinked polyethylene

Several techniques have been developed to obtain crosslinked polyethylene. Peroxide crosslinking, irradiation techniques and silane crosslinking are the three most common techniques. However, both peroxide and irradiation crosslinking techniques involve high investment costs[25]. Other drawbacks are the risk of pre-curing and high production cost during peroxide crosslinking and the thickness limitation in radiation crosslinking[25]. The silane crosslinking technique does not suffer from high investment cost and the silane grafted polyethylene can be processed and shaped in conventional thermoplastic processing equipment and subsequently crosslinked after the processing steps.

1.3.1. Silane crosslinking

Silane crosslinked polyethylenes are a commercial product for the global wire and cable market. The crosslinking takes place in the presence of trace amounts of water and the reactions can be accelerated by incorporating a tin-based catalyst. In the first step, the methoxyl groups are hydrolysed to hydroxyl groups during. The crosslinking takes place in the second step where the hydroxyl groups recombine through a condensation step[26], as shown in Figure 2. The schematic picture below shows the crosslinking mechanism for vinyltrimethoxy silane grafted onto the polyethylene backbone; however in the case of co-polymerised ethylene-vinyltrimethoxy silane, the silane trimethoxy group is coupled directly to the polyethylene backbone.

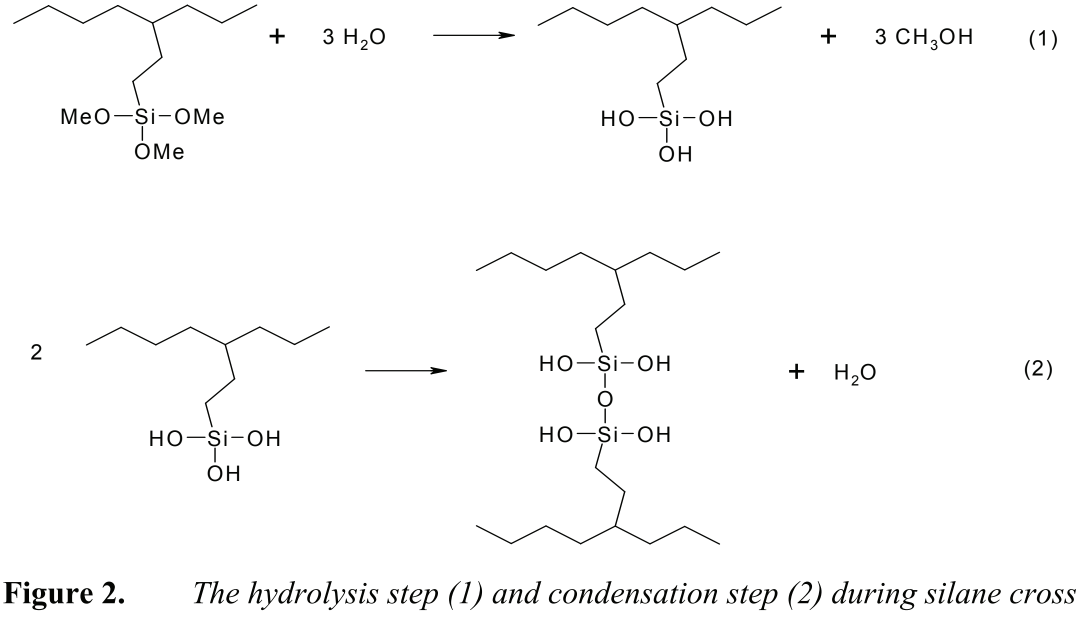

Figure 2. *The hydrolysis step (1) and condensation step (2) during silane crosslinking.*

1.3.1.1. Sioplas

Sioplas was the initial silane crosslinking technique and was introduced in the late 1960s by Dow Corning[27]. In the first step, vinyl silane is grafted onto polyethylene by means of small amounts of peroxide using reactive extrusion. The silane-grafted polyethylene is then pelletized and sold to downstream converters who generally add catalysts and other desired additives. After extrusion or moulding, the shaped product is crosslinked in a water bath or sauna at 80-90 ºC[26]. The Sioplas technique is often referred to as the "two step" process. Disadvantages with this method include the risk of premature crosslinking during storage and the risk of introduction of impurities during the two step procedure[27].

1.3.1.2. Monosil

The Monosil technique was developed by BICC in co-operation with Maillefer[27]. In this technology, polyethylene, peroxide, vinyl silane, catalyst and other additives are added in one continuous extrusion step. The single-step process combines the raw materials, accomplishes the grafting reaction and continuously forms a final product. As in the Sioplas technique, a water bath or sauna is needed to moisture-cure the material. Drawbacks associated with the Monosil are the higher investment cost and the increased technical complexity compared to the Sioplas technique[27].

1.3.1.3. Ethylene vinylsilane co-polymers

Ethylene vinylsilane copolymers are produced by free radical polymerisation in accordance with the original polyethylene polymerisation process (high pressure process)[28]. This technique was developed in the 1980s. In the polymerisation process, ethylene, minor amount of vinyl silane, and trace amounts of a radical initiator (e.g. oxygen) is fed into the reactor[28]. Once produced, the silane copolymers can be processed on conventional extruders together with a catalyst and other additives. As in the two other methods, the final product is moisture-cured. Advantages with this method include the high degree of cleanness in the reactor, no contamination with peroxide residues, and the lower level of silane needed[27].

1.4 Crosslinked wood-thermoplastic composites

There are only few reported studies on crosslinked wood-thermoplastic composites. Kuan et al.[29] studied silane crosslinked linear low-density polyethylene-wood flour composites. The wood flour was treated with vinyltrimethoxy silane before being compounded with polyethylene. The crosslinking was subsequently initiated by water treatment. Water crosslinked composites exhibited better mechanical properties than the non-crosslinked ones and this was attributed to being a result of chemical bonding between both wood and polyethylene. Other studies have used peroxides to crosslink composites of polyethylene/polypropylene and wood flour / pulp[30-32]. The mechanical properties of peroxide crosslinked composites were reported to be better than the non-crosslinked. Janigova et al.[30] showed that peroxide crosslinking improved the adhesion between the polyethylene and the wood filler as a result of recombination of radicals formed at the filler surface and polyethylene macro radicals. Moreover, Albano et al.[33] studied the effect of different doses of γ-irradiation on the mechanical properties of blends of polypropylene/high density polyethylene and wood flour. The results from the mechanical testing of the irradiated composites were rather complex and it was suggested that crosslinking and degradation occurred simultaneously.

1.5 Aim of study

Wood based material, such as wood fibres and flour, are interesting reinforcement for thermoplastics. Wood fibres provide advantages over conventional reinforcing materials; among these advantages are low cost, abundancy, renewability, and low specific gravity. In addition, wood fibres also have high specific strength and stiffness. Wood-thermoplastic composites are an alternative material for pressure-treated wood but can also replace engineering plastic products. Drawbacks of wood-thermoplastic composites are the poor interfacial adhesion between the hydrophilic wood fibres and the hydrophobic polymers which leads to decreased strength and impact properties. Other challenges for these materials include improving the long-term load performance and the durability during outdoor exposure.

The aim of this study was to develop silane crosslinked wood-thermoplastic composites with polyethylene as the matrix and wood flour as reinforcement. Silane crosslinking of the composites is believed to improve the long-term load performance and the durability during outdoor exposure. Moreover, if the wood flour is included in the network with chemical bonding to the polyethylene matrix, the interfacial adhesion between the wood and polyethylene will be improved. In this study, manufacturing of silane crosslinked wood-polyethylene composites was performed by reactive melt compounding. The composite materials were evaluated using chemical analysis, mechanical testing, spectroscopic analysis, thermal analysis, and electron microscopy.

2. Experimental

The composite materials were manufactured by melt compounding in a twin-screw extruder. There are a number of methods for studying the properties of composite materials. The composite materials were mechanically tested using tensile, flexural, creep and impact testing, but also with dynamic mechanical thermal analysis. Scanning electron microscopy (SEM) analysis was used to examine the fracture surface of the composites and electron probe microanalyzer (EPMA) was used to localise the silane in the composites. The degree of crosslinking in the samples was determined by gel content and swelling experiments and structural information of the crosslinking reaction was obtained by Fourier transform infrared spectroscopy (FTIR). Differential scanning calorimetry measurements were performed to determine the degree of crystallinity in the samples.

2.1 Materials

In all the studies, high-density polyethylene was used as the matrix and wood flour as the reinforcement. In paper I, a commercial vinyltrimethoxy silane grafted high density polyethylene was used as the matrix. In paper II-V, grafting of vinyltrimethoxy silane onto polyethylene/wood was performed during the melt compounding step. Small amounts of dicumyl peroxide were used to initiate the grafting reaction. A lubricant consisting of modified fatty esters was used during manufacture of profiles in paper V.

2.2 Processing

The wood flour was dried prior to melt compounding. Polyethylene granulates and wood flour were compounded using a co-rotating twin-screw extruder. The polyethylene and the wood flour were fed to the extruder by the use of gravimetric feeders. The temperatures and screw speed in the extruder during compounding were typically between 170-200 ˚C and 100-200 rpm, respectively. Silane crosslinked composites were produced by pumping a solution of vinyltrimethoxy silane and small amounts of dicumyl peroxide into the extruder at temperature zone 1. Vacuum venting was used to minimize volatile extractives and un-reacted silane in the final samples. A schematic picture of typical processing settings during melt-compounding of silane crosslinked composites is shown in Figure 3. Specimens for testing were cut directly from the extruded profiles or from subsequent compression moulded samples.

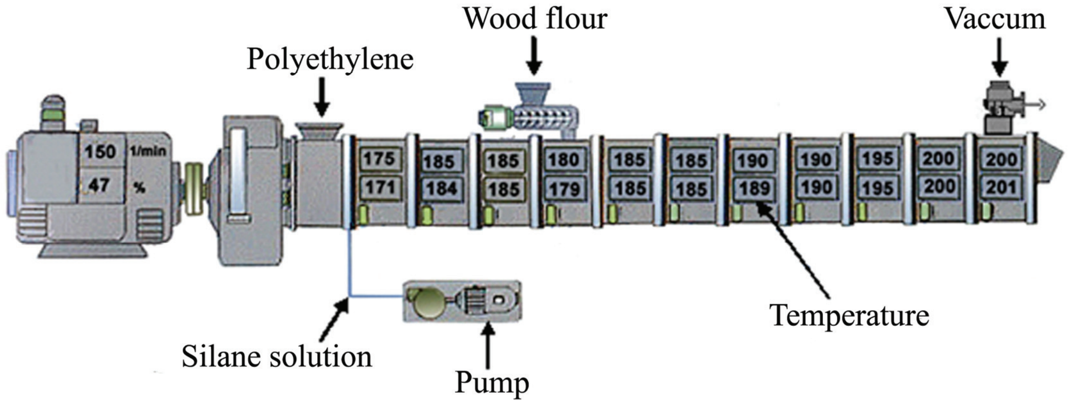

Figure 3. *Typical processing setting during melt compounding of crosslinked composites in a co-rotating twin screw extruder.*

2.3 Mechanical testing

2.3.1 Tensile and flexural properties

Tensile and flexural properties of the composites were measured with use of a miniature material tester (MiniMat) and by using conventional mechanical testing equipment. The tensile testing with MiniMat (Paper I) can only be used for internal comparison between the samples since the procedure was not in accordance with any standard. The flexural testing, on the other hand, was performed in accordance with ASTM-standard D790. Tensile and flexural stress, strain, and modulus were calculated according to the following equations:

Tensile testing:

$$\sigma = \frac{P}{A} \qquad (1)$$

$$\varepsilon = \frac{\Delta L}{L_0} \times 100 \qquad (2)$$

$$E = \frac{\Delta \sigma}{\Delta \varepsilon} \text{, initial linear part of the curve} \qquad (3)$$

σ = tensile stress (MPa), P = load (N), A = cross-section of beam (mm^2), ε = tensile strain (%), ΔL = elongation (mm), L_0 = original length (mm), E = tensile modulus (MPa)

Flexural testing:

$$\sigma = \frac{3 \times P \times S}{2 \times b \times d^2} \qquad (4)$$

$$\varepsilon = \frac{6 \times D \times d}{S^2} \times 100 \qquad (5)$$

$$E = \frac{S^3 \times m}{4 \times b \times d^3} \qquad (6)$$

σ = flexural stress (MPa), P = load (N), S = support span (mm), b = width of beam (mm), d = depth of beam (mm), ε = flexural strain (%), D = maximum deflection of the centre of beam (mm), E = flexural modulus (MPa), m = slope of the tangent to the initial straight-line portion of the load-deflection curve (N/mm)

2.3.2 Creep

Creep experiments were performed to study how the crosslinking affected the creep response in the composites. Creep is the time-dependent increase in strain of a material during constant loading. For the most general case of a linear viscoelastic material, the total strain e is the sum of three essentially separate parts: e_1 the immediate elastic deformation, e_2 the delayed elastic deformation and e_3 the Newtonian flow, which is identical to the deformation of a viscous liquid obeying Newton's law of viscosity[34]. The magnitudes of e_1, e_2 and e_3 are exactly proportional to the magnitude of the applied stress, so that a creep compliance $J(t)$ can be defined, which is the function of time only:

$$J(t) = \frac{e(t)}{\sigma} = J_1 + J_2 + J_3 \qquad (7)$$

where J_1, J_2 and J_3 corresponds to e_1, e_2 and e_3 [34]. Crosslinked polymers do not show a J_3 term, and to a very good approximation neither do highly crystalline polymers[34]. The creep modulus, E_c, represents the modulus of a material at a given stress level and temperature over a specified period of time. Creep modulus is expressed as the inverse of the creep compliance[34].

2.3.3 Impact testing

The impact strength of the composites was determined by Izod and instrumented drop weight impact testing to study the effect of crosslinking on the impact resistance. Impact strength is the ability of a sample to maintain its integrity and to absorb a sudden impact[34]. A material can absorb energy during impact through material deformation and creation of new surfaces[35]. The impact energy will initiate cracks at places with high stress concentration in the sample which then propagates through the material. There will be a continuous material deformation in advance of the crack when it propagates through the material. A stiff matrix will absorb less energy than a ductile matrix due to a larger material deformation in the ductile matrix[35]. Crosslinking of a brittle polymer will usually decrease toughness because of increased limitation of motion within the polymer mass caused by the intermolecular bonds, but crosslinking of a flexible polymer will increase impact toughness because of the greater ability of the polymer to transfer the energy[36]. The new areas created during crack propagation will absorb energy. Large crack areas may be produced by crack branching, in which case the cracks run in a direction normal to the general direction of the fracture[35]. The impact strength of filled polymers is usually lower than for unfilled because the more rigid filler acts as stress concentration. In general, a weak interface will be the weakest part of a short-fibre composite and provide a site for failure[15]. By improving the interfacial adhesion between the matrix and the filler, stress can be transferred from the matrix to the fibres thereby improving the impact strength[15]. Notched samples give information about crack propagation in the sample, while un-notched samples give information about crack initiation and propagation

2.3.4 Dynamic mechanical thermal analysis, DMTA

Dynamic mechanical thermal analysis (DMTA) was used to determine thermal transitions and how the mechanical properties of the samples varied with temperature. DMTA examines the behaviour of visco-elastic materials according to temperature and frequency-dependent behaviour. In dynamic mechanical measurements, the sample is subjected to a periodic sinusoidal stress (σ). The resulting strain (ε) is also sinusoidal with the same frequency, but with a lag in the phase[37], as shown in Figure 4 below:

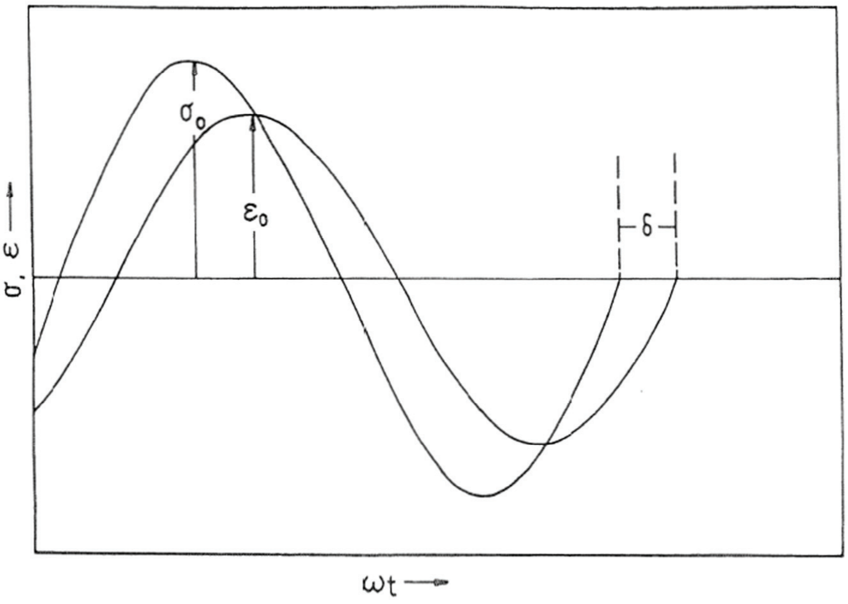

Figure 4. *Stress-strain relationships during DMTA-analysis*[37]

This phase lag is caused by energy absorption during loading and is expressed as an angle δ. The phase lag and amplitude of the curves can then be used to calculate the storage modulus E' and loss modulus E'' according to the following equations[38]:

$$\varepsilon = \varepsilon_0 \times \sin(\omega t) \qquad (8)$$

$$\sigma = \sigma_0 \times \sin(\omega t + \delta) \qquad (9)$$

Equation (9) can be re-written by the use of the trigonometric laws:

$$\sigma = \sigma_0 \left[\cos\delta \times \sin(\omega t) + \sin\delta \times \cos(\omega t)\right] \qquad (10)$$

Equation (10) can be re-written by introducing the storage modulus E' and loss modulus E'':

$$\sigma = \varepsilon_0 \left[E' \times \sin(\omega t) + E'' \times \cos(\omega t)\right] \qquad (11)$$

where E' and E'' are defined as:

$$E' = \frac{\sigma_0}{\varepsilon_0} \times \cos\delta \qquad (12)$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \times \sin\delta \qquad (13)$$

E' is a measure of the amount of energy that is recovered from the sample during every periodic cycle (elastic part). E'' is a measure of the amount of energy that is transformed to heat energy during every periodic cycle (viscous part). During a DMTA-temperature ramp test it is common to plot E', E'' and tan δ as a function of temperature where tan δ is defined as:

$$\tan\delta = \frac{E''}{E'} \qquad (14)$$

Figure 5 shows an example of a DMTA-analysis of a thermoplastic polymer. The glass-transition temperature (T_g) can be determined as the peak of the loss modulus E'' or the peak of tan δ [38]. However, it should be noted that even if DMTA can be used to characterize T_g, the motion of the molecular segments are frequency dependent and the most accurate T_g value is therefore measured by dilatometry.

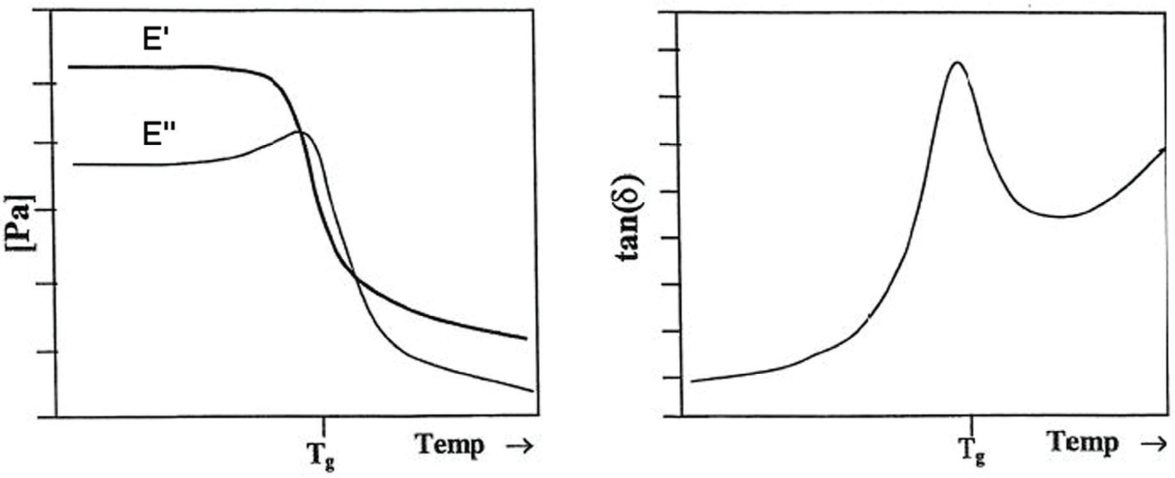

Figure 5. *Typical results from DMTA-analysis of a thermoplastic polymer. The graph to the left shows the storage and loss modulus as a function of temperature and the graph to the right shows tan δ as a function of temperature.*

2.4 Electron microscopy

2.4.1 Scanning electron microscopy, SEM

The morphology of the fracture surface of the composites was studied using scanning electron microscopy (SEM). SEM permits the observation and characterisation of heterogeneous organic and inorganic materials on a nanometer to micrometer scale[39]. In SEM, electrons are generated in a filament and then accelerated through a potential difference (1-40 kV), see Figure 6. The electrons pass through a column with lenses which de-magnify the beam (~ x 10 000) and focus it into a thin electron beam at the specimen (< 10 nm)[40]. Two pairs of electromagnetic scan coils are used to sweep the beam across the specimen until a rectangular raster is generated[39]. Simultaneously, the same scan generator creates a similar scan raster on the viewing screen. When the primary electrons hit the specimen, different signals will be generated that can be detected, see Figure 7. The signals of greatest interest are the secondary electrons, backscattered electrons and the characteristic X-ray signals. Secondary electrons are not a very accurate term that is used to describe those electrons which escape from the specimen with energies below about 50 eV [41]. Secondary electrons are abundant and are the most commonly used signal for surface topography imaging in SEM. Backscattered electrons are the primary electrons that leave the surface before having given up all their energy[41]. Backscattered electrons are not usually as numerous as secondary electrons but most of them carry high energy. They are also used for topography imaging but, in addition, can be used to obtain atomic number contrast and to yield diffraction contrast (crystallographic information)[40]. Detection of characteristic X-ray signals from the sample can be used to determine the chemical composition both qualitatively and quantitatively[40]. When the primary electrons have great enough energy, they can eject atom electrons from the K, L or M shell and thus leave the atom as an excited ion. The atom relaxes to its ground state by allowing outer shell electrons to fill the inner shell vacancy. The excess energy can then be released from the atom by the emitting characteristic X-ray or by emission of an Auger electron [39-40]. The wavelength of the characteristic X-ray is specific for atoms with a certain atomic number.

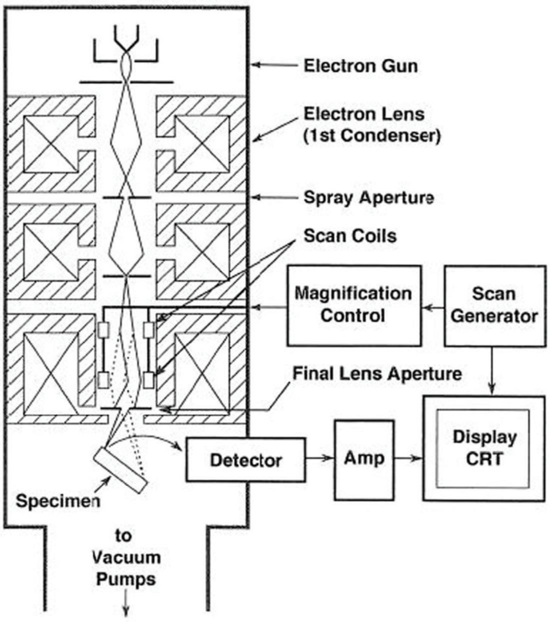

Figure 6. *Schematic drawing of a scanning electron microscope*[39].

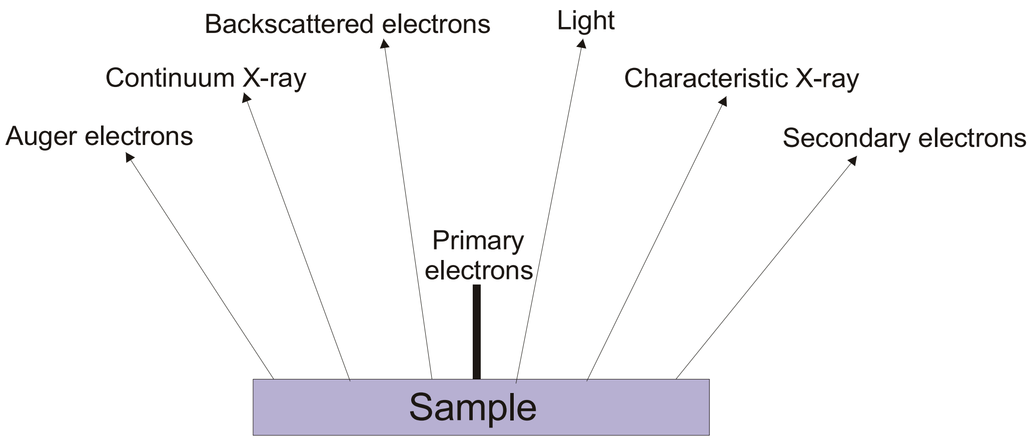

Figure 7. *Different signals that can be detected in SEM*[40].

2.4.2 Electron probe microanalyzer, EPMA

Electron probe microanalyzer (EPMA) was used to locate and map the silane in the crosslinked composites. An electron probe microanalyzer is basically a scanning electron microscope designed and optimized for X-ray analysis of elements from very small areas. A typical instrument is equipped with computer controlled crystal spectrometers, containing a range of crystals such that the whole spectrum can be covered[41]. The EPMA used in the study was equipped with four wavelength dispersive X-ray spectrometers and an energy dispersive X-ray spectrometer. This combination can simultaneously analyse up to 12 elements plus collect image signals from secondary and backscattered electrons.

2.5 Degree of crosslinking

The degree of crosslinking in the composites was determined by gel content and swelling experiments. Gel content and swell ratio was determined in accordance with ASTM standard 2765. The experimental setup for the experiments is shown in Figure 8. Crosslinked polyethylene is insoluble in boiling p-xylene while the non-crosslinked part is soluble. The gel content (insoluble fraction) can thus be determined gravimetrically after extraction in boiling p-xylene for 12 hours. The degree of crosslinking in the composites was also determined by measuring the swell ratio after extraction in hot p-xylene. A low swell ratio corresponds to a high network density, while a higher swell ratio corresponds to a lower network density. The swell ratio after extraction for 24 hours at 110 ºC in p-xylene could be determined by gravimetric measurements.

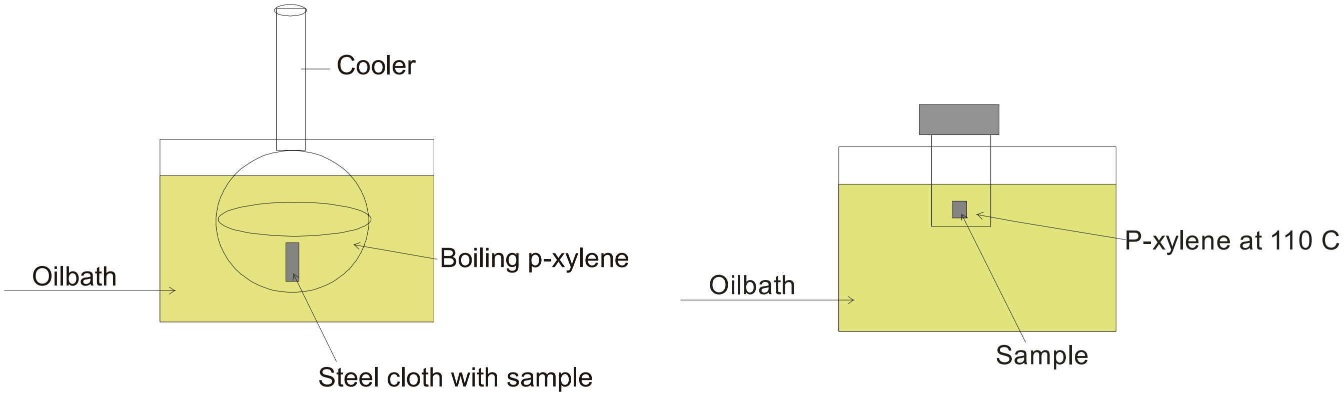

Figure 8. *Experimental setup during a) gel content and b) swelling experiments*

2.6 Fourier transform infrared spectroscopy, FTIR

Fourier transform infrared spectroscopy analysis was used to yield structural information about the crosslinking reaction in the composites. Almost any compound having covalent bonds, whether organic or in-organic, absorbs various frequencies of electromagnetic radiation in the infrared region of the electromagnetic spectrum. This region lies at wavelengths which range from approximately 400 to 800 nm[42]. In the absorption process, the frequencies of infrared radiation which match the natural vibration frequencies of chemical bonds in the molecule are absorbed. The instrument produces a beam of infrared radiation which is divided into two parallel beams, where the sample is placed in one beam and the other beam is used as reference. The wavelength of the radiation absorbed provides structural information of the chemical bonds in the sample.

2.7 Differential scanning calorimetry, DSC

The degree of crystallinity in the samples was determined by the use of differential scanning calorimetry measurements (DSC). This type of DSC instrument includes two heating discs which are in thermal contact with one another and are isolated from the environment. A metal pan is placed on each disc. One of the pans contains a sample and the other is an empty reference pan. The pans are then heated at a known rate and the heat flow needed to keep the two pans at the same temperature is measured. DSC allows users to measure thermal transitions in materials. Temperatures and quantities of heat can be measured for melting and solidification, glass transitions, and other phase changes. The melting enthalpy (endothermic process) can be used to calculate the degree of crystallinity in a polyethylene sample according to the following equation:

$$Crystallinity\ (\%) = \frac{\Delta H_{melting,\ sample}\ (J/g)}{\Delta H_{melting,\ 100\%\ crystalline\ polyethylene}\ (J/g)} \qquad (15)$$

A melting enthalpy of 290 J/g for 100 % crystalline polyethylene was used in the calculation of crystallinity[43].

3. Summary of appended papers

Paper I.

The effect of crosslinking on the properties of polyethylene/wood flour composites.

In this study the possibility of using silane technology in crosslinking composites of wood flour and polyethylene was investigated. Composites of vinyltrimethoxy silane grafted high density polyethylene and wood flour were produced by compounding in a twin-screw extruder. Gel content analysis with p-xylene extraction revealed higher gel content in the samples where wood flour was added, compared to samples with a neat crosslinked matrix. Mechanical analysis of the crosslinked composites showed increased tensile strength with increasing amount of wood flour, which might be an indication of improved adhesion between the matrix and the wood flour. The stiffness increased with an increasing amount of wood flour; this was accompanied by a decrease in strain at break. Dynamic mechanical thermal analysis of crosslinked plastics and composites showed no significant shift in the γ-transition towards higher temperatures for the composites than for neat plastic. Short-term creep experiments showed reduced creep deformation with an increasing amount of wood flour. Crosslinking of the composites reduced the creep deformation further. A boiling test in water followed by tensile testing showed that the crosslinked composites were less susceptible to water uptake than were the non-crosslinked composites. Moreover, the decrease in tensile strength of the crosslinked composites was not as significant as for the non-crosslinked composites. Scanning electron microscopy revealed good compatibility and adhesion between the plastic and the wood flour for crosslinked composites.

Paper II.

The use of silane technology in crosslinking polyethylene/wood flour composites.

In this study the use of silane technology in crosslinking polyethylene-wood flour composites was investigated. Composites were produced in a one step process using a co-rotating twin-screw extruder. The composites were stored in a sauna and at room temperature to study the effect of humidity on the degree of crosslinking. Crosslinked composites showed improved toughness and creep properties compared to non-crosslinked composites. The flexural modulus, on the other hand, was lower in the crosslinked samples than in the non-crosslinked ones. FTIR was used to study the crosslinking reaction in the samples. X-ray mapping of the silicon signal was also performed to locate the silane in the composites. This study provides a basis for proposing that part of the silane is grafted onto polyethylene and wood, thereby creating a crosslinked network in the matrix with chemical bonds (covalent and hydrogen bonding) to wood. The other part of the silane remains un-reacted and blends into the system.

Paper III.
Silane crosslinked wood plastic composites: Processing and properties.

The focus of the study was to produce silane crosslinked wood plastic composites in a compounding process. Silane crosslinking is one way to improve the mechanical and long-term properties of wood plastic composites. Silane crosslinked composites with different amounts of vinyltrimethoxy silane were produced in a compounding process using a co-rotating twin-screw extruder. The composites were stored in a sauna and at room temperature to study the effect of humidity on the degree of crosslinking. Gel content and swelling experiments showed that the highest degree of crosslinking was found in the composites stored in a sauna. The crosslinked composites showed toughness, impact strength and creep properties superior to those composites to which no silane was added. The flexural modulus, on the other hand, was lower in the crosslinked samples than in the non-crosslinked ones. Differential scanning calorimetric measurements of the composites showed a lower crystallinity in the crosslinked samples than in the non-crosslinked.

Paper IV.
Optimization of silane crosslinking technology for use in polyethylene/wood flour composites.

The aim of the study was to optimise the silane crosslinking technology for use in polyethylene/wood flour composites. Silane crosslinked wood-polyethylene composites with 0, 2, 3, 4, and 6 % of added silane solution were produced in a one-step compounding process. The composites were stored in a sauna at 90 ºC and at ambient conditions. Gel content and swelling data showed the highest degree of crosslinking in the sauna-stored composites. An addition of at least 4 % of silane solution during processing was necessary to fully crosslink the composites in the sauna within 48 hours. The crosslinked composites showed toughness and creep properties superior to those composites to which no silane was added. The flexural strength of the crosslinked composites reached a maximum of between 2-3 % w/w of added silane and then decreased with further addition of silane. Moreover, the flexural modulus was lower in the crosslinked samples than in the non-crosslinked. Differential scanning calorimetric measurements of the specimens showed a lower crystallinity in the crosslinked samples than in the non-crosslinked. A linear relationship between the flexural modulus and the crystallinity in the composites was found.

Paper V.

Profile extrusion and mechanical properties of crosslinked wood-thermoplastic composites.

Challenges for wood-thermoplastic composites to be utilized in structural applications are to lower product weight and to improve the long-term load performance. Silane crosslinking of the composites is one way to reduce the creep during long-term loading and to improve the mechanical properties. In this study, silane crosslinked wood-polyethylene composites were produced by reactive extrusion and subsequently manufactured into rectangular profiles. The silane crosslinked composites were stored in a sauna at 90 ºC to increase the degree of crosslinking. The toughness of the silane crosslinked composites was significantly higher than for the non-crosslinked composites. Improved adhesion between the wood and polyethylene phases is the most likely reason for the improved toughness of the crosslinked composites. There was no significant difference in flexural modulus between the crosslinked and non-crosslinked composites. In addition, impact testing showed that the impact strength of the crosslinked composites was considerably higher (at least double) than the non-crosslinked. The effect of temperature on the impact strength of the composites indicated slightly higher impact strength at -30 ºC than at 0º and at 25 ºC, and then an increase in impact strength at 60 ºC. Crosslinking also reduced the creep response during short-term loading. Moreover, scanning electron microscopy on the fracture surface of the crosslinked composites revealed good adhesion between the polyethylene and wood phases.

4. Conclusions

Silane crosslinked polyethylene-wood flour composites were successfully manufactured by reactive compounding in a twin-screw extruder. In the first study, a commercial silane grafted polyethylene was melt blended with wood flour. In the following studies, compounding of polyethylene and wood flour and silane grafting were carried out simultaneously. Addition of silane solution during compounding increased the melt viscosity as a result of premature crosslinking and interaction between grafted silane groups. The increase in melt viscosity caused edge-tearing and a rough surface of the crosslinked profiles when no lubricant was used. However, the use of lubricant removed the rough surface and the edge-tearing of the composites.

Gel content and swelling experiments showed that the crosslinking reaction was initiated already during compounding. An increased level of silane addition and wood flour content during compounding increased the degree of premature crosslinking. It was shown that an addition of 4 % w/w or more of the silane solution during processing was necessary to fully crosslink the composites in a sauna within 48 hours. Storage at ambient conditions did not significantly affect the degree of crosslinking in the composites. However, storage in a high humidity sauna significantly increased the degree of crosslinking in the composites. Fourier transform infrared spectroscopy analysis of the crosslinked composites showed peaks corresponding to both un-hydrolysed $Si-O-CH_3$ groups and polysiloxanes (Si-O-Si). In the crosslinked composites stored in sauna with higher degree of crosslinking, peaks corresponding to polysiloxanes (Si-O-Si) were more prevalent.

The crosslinked composites showed tensile/flexural strength and strain superior to the composites to which no silane was added. In addition, the strength increased with an increasing amount of wood flour. Improved adhesion between the wood and the polyethylene matrix is most likely the reason for the significant improvement in toughness of the crosslinked composites. The flexural strength of the crosslinked composites reached a maximum between 2-3 % w/w of added silane and then decreased with further addition of silane. There was no significant difference in flexural modulus between the non-crosslinked and the crosslinked composites when the silane addition was low (2-3 %). However, at a higher level of silane addition, the flexural modulus of the crosslinked composites was lower than for the non-crosslinked composites. Differential scanning calorimetric measurements of the composites showed a lower crystallinity in the crosslinked composites than in the non-crosslinked composites. The crystallinity was also found to decrease with an increased amount of added silane during compounding. A decrease in crystallinity at higher level of silane addition is thus believed to explain the lowering in modulus and strength. Furthermore, short-term creep analysis showed that the creep response in crosslinked composites was significantly lower than in the non-crosslinked composites. The lower creep in the crosslinked composites was related to a reduced viscous flow due to crosslinking, as well as to improved adhesion between the polyethylene matrix and wood flour. There was a good correlation between the creep response and the degree of crosslinking in the composites. A higher degree of crosslinking in the composites lowered the creep response. Creep analysis at elevated temperature also showed that the crosslinked composites were less affected by the temperature than were the non-crosslinked composites. Impact testing showed that the impact strength of the crosslinked composites was considerably higher than the non-crosslinked composites. Improved adhesion between wood and polyethylene and improved impact strength of the polyethylene matrix upon crosslinking can explain the superior impact strength of the crosslinked composites.

Scanning electron microscopy on the fracture surface of the crosslinked composites showed no gap between polyethylene and wood, indicating good interfacial adhesion. Moreover, the crosslinked composites showed almost no signs of fibre pull-outs and most of the fibres were fractured. X-ray microanalysis of the composites showed that most of the silane was found in close proximity to the wood fibre, both around and inside the wood fibres. It was also possible to locate silane evenly spread out in the matrix. A boiling test in water followed by tensile testing was used as an indirect measurement of interfacial adhesion between the polyethylene and wood fibres in the composites. The boiling test showed that the crosslinked composites were less susceptible to water uptake than were the non-crosslinked composites. In addition, the decrease in tensile strength of the crosslinked samples after boiling was not as significant as for the non-crosslinked composites.

5. Future work

This study has shown that silane crosslinking of polyethylene-wood flour composites improved their toughness, impact strength, creep performance and water resistance. A reactive extrusion process was developed where compounding of polyethylene and wood flour and silane grafting were carried out simultaneously. The reactive extrusion is rather simple to perform from a practical standpoint since it is a matter of adding small amounts of vinyl silane solution during melt compounding. However, there are many factors that can influence the grafting efficiency of silane onto polyethylene/wood, such as mixing efficiency, temperature, pressure, residence time, venting, type of polyolefin used, monomer, initiator, screw/extruder design. Some of these factors have been investigated but others are still to be investigated further. For commercialization purposes it would also be necessary to optimize the rheology and surface properties during larger scale manufacturing of silane crosslinked composite products. Possible variation in the degree of crosslinking over the thickness of larger scale products has not been studied and would be interesting to evaluate. It would also be interesting to investigate the potential of silane crosslinking on other types of composite systems with other thermoplastic matrices and natural fibres. Moreover, a comparison between silane, peroxide, and irradiation crosslinking techniques on the properties of wood-thermoplastic composites would be interesting to carry out.

Although wood-thermoplastic composites are promoted as high durability products, accelerated weathering studies have shown that the composites experience a colour change and loss in mechanical properties. Currently, silane crosslinked composites are being subjected to accelerated weathering. Evaluation of the results from that experiment will reveal if silane crosslinking can improve the durability of wood-thermoplastic composites during outdoor exposure.

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Paper I

The effect of crosslinking on the properties of polyethylene/wood flour composites

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The effect of crosslinking on the properties of polyethylene/wood flour composites

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Abstract

In this study, the possibility of using silane technology in crosslinking composites of wood flour and polyethylene has been investigated. Composites of vinyltrimethoxy silane grafted high density polyethylene and wood flour were produced by compounding in a twin-screw extruder. Gel content analysis with *p*-xylene extraction revealed higher gel content in the samples where wood flour was added compared to neat crosslinked matrix. Mechanical analysis of the crosslinked composites showed increased tensile strength with increasing amount of wood flour, which might be an indication of improved adhesion between the matrix and the wood flour. The stiffness increased with increasing amount of wood flour with accompanied decrease in strain at break. Dynamic mechanical thermal analysis of crosslinked plastics and composites showed no significant shift in the γ-transition towards higher temperature for the composites compared to neat plastic. Short-term creep experiments showed reduced creep deformation with increasing amount of wood flour. Crosslinking of the composites reduced the creep deformation further. A boiling test in water followed by tensile testing showed that the crosslinked composites were less susceptible to water uptake compared to the non-crosslinked. Moreover, the decrease in tensile strength of the crosslinked composites was not as significant as for the non-crosslinked composites. Scanning electron microscopy revealed good compatibility and adhesion between the plastic and the wood flour for crosslinked composites.

Keywords: A. Short-fibre composites; B. Durability; B. Creep; D. Scanning Electron Microscopy (SEM); Crosslinking

1. Introduction

Composite materials are created by combining two or more components to achieve desired properties which could not be obtained with the separate components. Wood-based composites using thermoplastics as a continuous phase can result in better water resistance and dimensional stability compared to composites with low polymer content [1]. Wood-based composites with a continuous thermoplastic phase also give the opportunity to process the composite using conventional thermoplastic processing equipment [2]. These composites can be used to replace impregnated wood in many outdoor applications but can also be used as replacement for neat plastics. There are environmental and economical reasons for replacing part of the plastics with wood but the wood could also work as reinforcement of the plastics. The elastic modulus of wood fibres is approximately 40 times higher than that of polyethylene and the strength about 20 times higher [3].

The increased interest in the use of wood as filler and/or reinforcement in thermoplastics is due to the many advantages. Low density, high stiffness and strength, and low price are some of these advantages [4–7]. The environmental awareness of people today is forcing the industries to choose natural materials as substitutes for non-renewable materials. Wood has been used as

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building and engineering material since early times and offers the advantages of not just being aesthetically pleasing but also renewable, recyclable and biodegradable [8]. Moreover, the processing of wood composites minimizes abrasion of the equipment due to the low hardness of wood compared to the inorganic fillers used in a great amount before [5]. In spite of all the advantages mentioned above, there are also some drawbacks in using wood fillers as reinforcement in thermoplastics. The main drawbacks are the difficulties of achieving good dispersion and strong interfacial adhesion between the hydrophilic wood and the hydrophobic polymers which leads to composites with rather poor durability and mechanical properties [5,6,9–11].

Many different modifications of thermoplastic wood composites have been tested and the basic role of these modifications is to reduce wood–wood interactions and increase wood–polymer interactions. Numerous studies have used graft copolymers of synthetic polymers (e.g., PP and PE), and maleic anhydride (MA) as coupling agents for thermoplastic wood composites [5,10–14]. The coupling agent (MA-PP or MA-PE) can modify the interface by interacting with both the filler and the matrix, thus forming a link between the components [12]. Kokta et al. [9] and Raj et al. [15] studied the use of polymethylene-polyphenyl-isocyanate (PMPPIC) as a coupling agent in thermoplastic wood composites. The addition of PMPPIC to the composites improved the mechanical properties compared to unmodified composites. Kokta et al. [9] and Raj et al. [15] also studied the use of silanes as coupling agents in thermoplastic wood composites. Special preparation methods were used for coating the filler with silane (e.g., use of different solvents) and different kind of additives (e.g., benzoyl and dicumyl peroxide). These special treatments were necessary to achieve improved mechanical properties comparable (mostly lower) to those where, e.g., PMPPIC was used as a coupling agent. Several studies have also been performed with the aim of improving the ductility and impact strength of thermoplastic wood composites [6,14,16]. In the study of Oksman and Clemons [14] different modifiers (compatibilizers and impact modifiers) were investigated. Most promising was maleated styrene–ethylene–butadiene-styrene (MA-SEBS), which was found to act, not only as compatibilizer but also as impact modifier.

Another way of modifying thermoplastic wood composites is crosslinking. Janigova et al. [17] showed improved adhesion in peroxide crosslinked composites of wood flour filled LDPE compared to non-crosslinked ones. The improved adhesion was explained as a result of covalent bonding between the wood and the LDPE-matrix. The bonding was believed to be created as a result of recombination of radicals formed at the filler surface (after attack of peroxide oxy radicals) and polyethylene macroradicals. SEM-pictures showed a clear sign of de-wetting on the filler surface for non-crosslinked composites while patterns of fracture through the filler were visible for crosslinked composites. Sapieha et al. [18] proposed the same mechanism responsible for improved adhesion in crosslinked composites of LLDPE and bleached hardwood pulp. Sain and Kokta [19] studied composites of polypropylene (PP) and thermosetting resin (epoxy and phenolic) – coated cellulosic fibres. Maleic anhydride graft-PP was used as compatibilizing agent. Such compatibilized thermoplastic–thermoset composites were found to have tensile strength higher than that of unfilled PP and tensile toughness about as good as that of PP.

In this study, the possibility of using silane technology in crosslinking composites of wood flour and polyethylene has been investigated.

2. Experimental

2.1. Materials

Vinyltrimethoxy silane grafted high density polyethylene, BorPex HE2515 (MI = 1 g/10 min, 190 °C/5 kg) and HDPE MG7547 (MI = 4 g/10 min, 190 °C/2.16 kg) was purchased from Borealis AB (Stenungsund, Sweden). According to the supplier, the amount of vinyltrimethoxy silane in BorPex was approximately 2% (w/w). Mechanical data of the plastics according to the supplier is shown in Table 1. It should be noticed that the mechanical data of BorPex is for non-crosslinked sample. Wood flour from softwood (spruce and pine) was kindly provided of Scandinavian Wood Fiber AB (Orsa, Sweden). According to the supplier, the size of the softwood wood flour was 200–400 μm. The shape of the wood flour was fractured fibre bundles. Throughout the paper, the crosslinked polyethylene (BorPex) is referred to as "XLPE" and the non-crosslinked (HDPE MG7547) as "HDPE".

2.2. Wood flour size distribution

The wood flour size distribution was determined using an Analysette 3 Spartan automatic vibratory sieve shaker (Laval Lab Inc., Quebec, Canada). The device

Table 1
Mechanical data of the plastics according to the supplier

Plastic	Tensile stress at yield (MPa)[a]	Modulus of elasticity (MPa)[b]	Elongation at break (%)[a]
BorPex HE2515 (XLPE)	27	960	195
HDPE MG7547 (HDPE)	24	950	–

[a] 50 mm/min.
[b] 1 mm/min.

was equipped with the following sieves; 1000, 315, 100, 50 and 20 μm. Wood flour (100 g) was placed on top of the 1000 μm sieve and then vibrated at 50–60 Hz for 10 min. The amount of wood flour on each sieve after vibration was determined gravimetrically. The wood flour size distribution was taken as the average of five different measurements.

2.3. Processing

The wood flour was dried for 24 h at 100 °C to a moisture content of 2.2% (based on dry weight) before processing. Plastic granulates and wood flour were compounded using a Coperion Werner and Pfleiderer ZSK 25 WLE (Stuttgart, Germany) corotating twin-screw extruder. The barrel temperatures were; 175 °C for zone 1, 185 °C for zones 2 and 3, 180 °C for zone 4, 185 °C for zones 5 and 6, 190 °C for zones 8 and 9, 195 °C for zone 9, and 200 °C for zones 10 and 11. The screw speed was 150 rpm, the pressure at the die varied between 28 and 70 bar depending on material blend, and the material output was 4 kg/h. Feeding of the wood flour was performed at temperature zone 4 through a twin-screw side feeder operating at 150 rpm. Vacuum ventilation was used to minimize the moisture content during processing. The extruded strands were directly transported between two cooled and rotating metal rollers and thus pressed into bands with a thickness of approximately 1 mm. The compositions of the different samples are shown in Table 2.

2.4. Crosslinking

After processing, the extruded bands of film were stored at ambient conditions for 5 weeks. The temperature and humidity during storage varied between 22 and 25 °C and 32% and 39%, respectively. After storage the samples were stored in a freezer at −10 °C to inhibit further crosslinking.

Table 2
Compositions of the different composites and plastics

Sample	Wt%		
	XLPE	HDPE	Wood flour
1	100	–	–
2	80	–	20
3	70	–	30
4	60	–	40
5	–	100	–
6	–	80	20
7	–	70	30
8	–	60	40

2.5. Gel content

The gel content of the plastics and composites was determined using *p*-xylene extraction according to ASTM standard 2765. The specimens to be analysed were ground and placed in folded 120 mesh stainless steel cloth cages. Cages with ground sample were weighed before immersion in the *p*-xylene. Butylated hydroxytoluene (BHT) was used as antioxidant to inhibit further crosslinking 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 to a constant weight was attained and subsequently re-weighed. The gel content of the different blends was determined as the average of two separate analyses. The gel-content was calculated according to the following equation:

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

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

2.6. Density measurement

The density of the neat plastics (non-crosslinked and crosslinked) was measured according to ASTM D790-00. The samples were immersed in air-free distilled water and the amount of displaced water was measured with an analytical balance. At least three specimens of each blend were tested. The specific density of the plastics was calculated as follows:

$$\text{sp gr } 23/23\ ^\circ\text{C} = a/(a + w - b), \qquad (2)$$

where a is the apparent mass of specimen in air (without wire or sinker); b is the apparent mass of specimen and of sinker completely immersed and of the wire partially immersed in water; w is the apparent mass of totally immersed sinker and of partially immersed wire.

The density of the plastics was calculated as follows:

$$D^{23C} = \text{sp gr } 23/23\ ^\circ\text{C} \times 997.5\ (\text{kg/m}^3). \qquad (3)$$

2.7. Mechanical testing

Tensile testing of the samples was performed on a Rheometric Scientific miniature materials tester Mini-Mat 2000 (Piscataway, NJ). The measurements were performed at ambient conditions, i.e., a temperature of 22 °C and a relative humidity of 39%. Rectangular samples measuring 1 × 5 × 80 mm were tested in tensile at a rate of 3 mm/min. The relative stress at maximum load, strain at failure, and modulus were calculated from the obtained stress–strain curves. Ten specimens of each blend were tested.

Dynamic mechanical thermal analysis measurements were carried out on various composites and neat plastics using a Rheometrics Dynamic Mechanical Thermal Analyzer DMTA V (Rheometric Scientific, Piscataway, NJ). The measurements were performed in tensile mode on specimens measuring approximately 1 × 8 × 30 mm. The strain and frequency were kept constant at 0.01% and 1%, respectively, during temperature ramp tests (2 °C/min) in a temperature interval from −145 °C to the melt peak.

Short-term creep experiments of composites and neat plastics were performed on the same DMTA instrument to measure the deformation as a function of time. The tests were carried out in tensile mode with specimens measuring approximately 1 × 5 × 15 mm. The applied static stress was 2 MPa and the temperature was fixed at 30 or 60 °C.

2.8. Boiling test

A boiling test was performed by immersing composite samples in boiling water for 2 h. Rectangular samples with the same dimensions (1 × 5 × 80 mm) as in the tensile testing were used. The samples to be analysed were first put in a desiccator until the water content was less than 0.5%. The samples were subsequently weighed before immersion in water and after the boiling the surface water was removed and the samples weighed again. Tensile testing of the samples after boiling was performed using the same procedure as described in the mechanical testing Section 2.6. Before tensile testing, the samples were reconditioned in a desiccator to the initial weight they had before immersion in water.

2.9. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to monitor the fracture surface of the composites after quenching the samples in liquid nitrogen. SEM analysis was performed using a Cambridge 360 (Cambridge, England). The samples were sputtered with a layer of gold/palladium before the measurements.

3. Results and discussion

3.1. Wood flour size distribution

The wood flour size distribution (WFSD) was determined using an automatic vibratory sieve shaker. As can be seen in Fig. 1, the major part of the wood flour is between 100 and 1000 μm, with two-thirds of the wood flour larger than 300 μm. According to the supplier, the size of the wood flour should be 200–400 μm. It can be concluded from the measurements that a very small part (4.2% (w/w)) of the wood flour was between 100 and 20 μm and hardly any wood flour had a size smaller than 20 μm or larger than 1 mm.

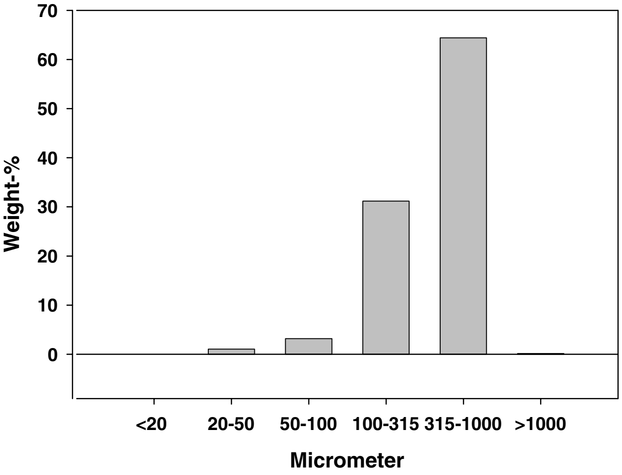
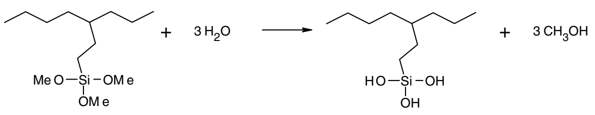


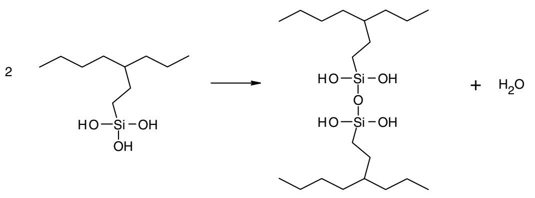
Fig. 1. Wood flour size distribution of the softwood used in the composites.

3.2. Crosslinking

Crosslinkable ethylene–vinyl silane copolymers are a commercial product for the global wire and cable market. The crosslinking takes place in the presence of trace amounts of water and the reactions can be accelerated by incorporating a tin-based catalyst. In the first step, the methoxyl groups are hydrolysed to hydroxyl groups during leaving of methanol. The crosslinking takes place in the second step where the hydroxyl groups recombine through a condensation step [20].



(1)



(2)

This is an introductive study where the goal was to investigate if the hydroxyl groups created in step (1) could react with hydroxyl groups in wood as well with other hydroxyl groups grafted on the polyethylene backbone, see Fig. 2. Formation of a network with covalent bonds between wood and polyethylene would improve the interfacial adhesion and improve the mechanical properties of the composites. Crosslinking could also

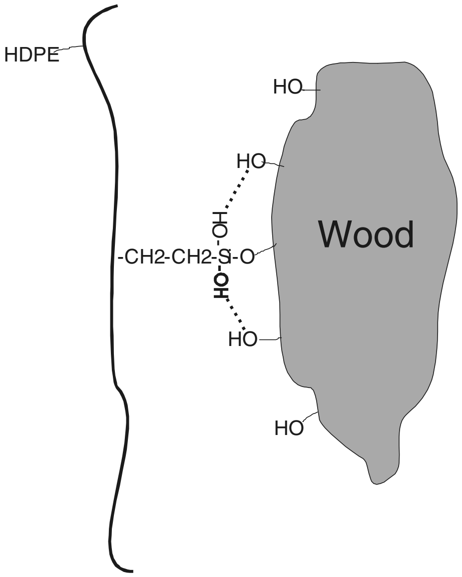


Fig. 2. Possible covalent and/or hydrogen bonding between wood and vinyltrimethoxy silane-grafted-HDPE.

lead to a stabilization of the morphology improving the long-term properties compared to non-crosslinked composites [21]. Moreover, crosslinked composites also give the possibility of utilizing mixtures of polymeric scrap eventually leading to useful materials [21].

The extruded bands of film were stored at ambient conditions for 5 weeks. The rate of the crosslinking reaction can be increased by incorporation of a tin-based catalyst (dibutyl-tin-dilaurate, DBTDL) during processing [20]. Incorporation of such catalyst would increase the rate of crosslinking of the plastic but could on the other hand counteract the reaction with wood. DBTDL has been shown to increase the rate of both the reaction steps in the crosslinking, i.e., hydrolysis and condensation [20]. In the presence of DBTDL, formation of an ether bond between plastic and wood (–Si–O–Wood) could be catalyst back to a silanol group.

3.3. Gel content

The gel content of neat XLPE and composites with XLPE as continuous phase was determined using *p*-xylene extraction according to ASTM standard 2765. Crosslinked polyethylene is insoluble in boiling *p*-xylene while the non-crosslinked part is soluble. The gel content can thus be determined gravimetrically from the extracted samples. As can be seen in Table 3, the gel content is higher in the composites compared to the neat XLPE. Wood is hygroscopic, that is it will absorb moisture from the atmosphere if it is dry and correspondingly yield moisture to the atmosphere when wet, thereby attaining a moisture content which is in equilibrium with the vapour pressure of the surrounding atmosphere [22]. The first step in the crosslinking reaction is hydrolysis of the methoxyl groups to silanol groups. A higher moisture content in the wood flour filled plastics compared to the neat plastic could thus explain the higher gel content. Extraction of neat wood flour resulted in a reduction of 5 wt% of the original mass, probably due to dissolution of extractives and soluble lignin.

Table 3
Gel content of neat XLPE and composites with XLPE as continuous phase

	Wood content (wt%)			
	0	20	30	40
Gel content	25	39	50	45

3.4. Mechanical testing

3.4.1. Tensile testing

In Fig. 3, typical engineering stress–strain curves for neat XLPE and composites with XLPE as continuous phase is shown. As can be seen in Fig. 3, the material becomes stiffer with the addition of wood flour with accompanied decrease in strain at failure. The sample with neat XLPE did not break during the measurement and the experiment was stopped at a strain level of 20%.

More interesting is the significant increase in tensile strength with increasing amount of wood flour. Without interfacial adhesion, between the wood and the plastic, the tensile strength would decrease with increasing wood flour content, as reported by many authors [4,7,9,17]. However, when crosslinking by silanes the polymer is in its solid state, and the crosslinks are located mainly in the amorphous regions and the crystalline structure is maintained [20]. Crosslinking of the amorphous regions of the polymer leads to a stronger material. Kuan et al. [23] showed that upon crosslinking, the tensile strength was only lifted 5.5–6.7%, compared to the

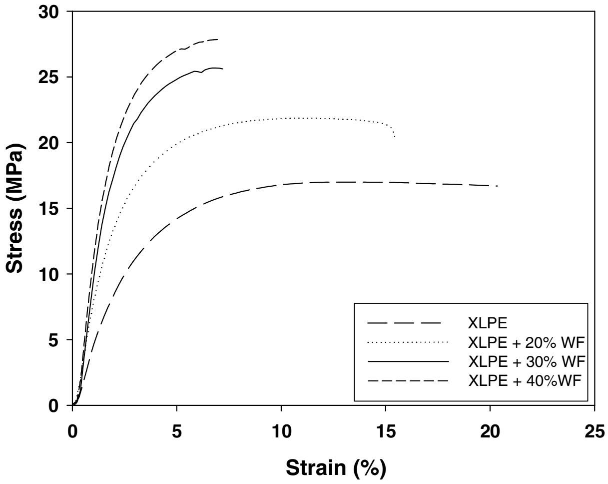


Fig. 3. Typical engineering stress–strain curves of neat XLPE and composites with XLPE as continuous phase.

silane-grafted-HDPE. Unfortunately, the gel content of the samples in these studies was not determined. Hjertberg et al. [20] showed that the ultimate strength of VTMS-LDPE was not significantly affected during treatment in water bath at 90 °C for 243 h. However, the elongation at break decreased initially as a natural consequence of crosslinking, but a constant level around 40% of the original one was reached after about 100 h. The gel content of these samples reached a maximum of 70–75% after 25 h and dibutyl-tin-dilaurate (DBTDL) was incorporated in the sample to catalyse the crosslinking reaction.

The gel content of the plastic and composites in this study varied significantly. The gel content was higher in the composites compared to neat XLPE. This could thus explain the increase in tensile strength with increasing wood content. On the other hand, the highest gel content was found in the composite with 30% wood flour but there was still an increase in tensile strength for the composite with 40% wood flour. An increase in tensile strength with 38%, when comparing the composite with 40% wood flour and neat XLPE, is much higher than the previously reported increment in tensile strength due to crosslinking. This is an indication of interaction between wood and plastic with accompanied transfer of stress from the weaker plastic phase to the wood through the interface.

The average values of the relative tensile strength and modulus for the crosslinked samples are shown in Figs. 4 and 5, respectively. The tensile strength and modulus values are normalised to that of neat XLPE. As can be seen in Figs. 4 and 5, the tensile strength and modulus is almost increasing linearly with increased wood flour content. According to Bigg as reported by Maldas et al. [24], the modulus is strongly affected by the filler level and the orientation of the filler and less by the polymer–fibre adhesion.

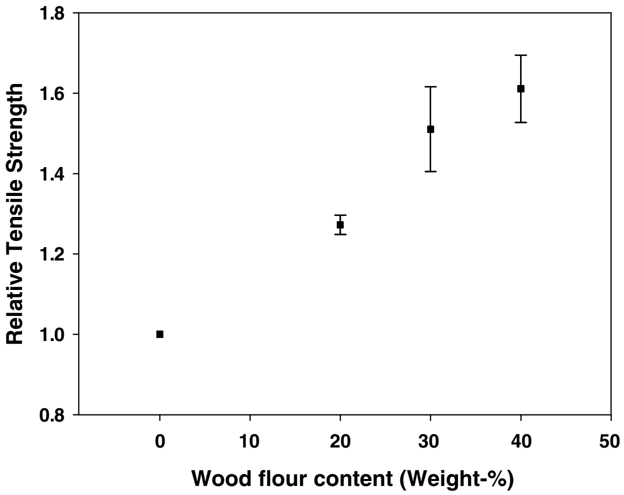


Fig. 4. Average values of the relative tensile strength as a function of wood content. The tensile strength values are normalised to that of neat XLPE.

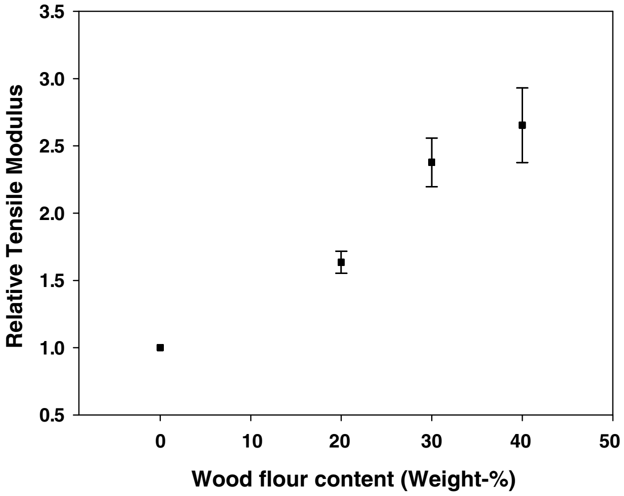


Fig. 5. Average values of the relative tensile modulus as a function of wood flour content. The modulus values are normalised to that of pure BorPex.

Mechanical data of the plastics and composites are summarised in Table 4. Mechanical data of non-crosslinked HDPE composites are also included in Table 4 for comparison. As can be seen in Table 4, the modulus of non-crosslinked HDPE is increasing with increased amount of wood flour. The tensile strength, on the other hand, is decreasing with increased amount of wood flour as would be expected in a composite with weak interfacial adhesion. In Fig. 6, a comparison of

Table 4
Mechanical data of different plastics and composites

Sample	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
XLPE	558.4 ± 53.6	16.9 ± 0.5	195[b]
XLPE + 20% WF[a]	912.7 ± 48.0	21.5 ± 0.4	17.0 ± 2.0
XLPE + 30% WF	1327.6 ± 101.0	25.6 ± 1.8	8.7 ± 1.8
XLPE + 40% WF	1481.5 ± 155.1	27.3 ± 1.4	6.9 ± 1.5
HDPE	694.3 ± 31.9	19.1 ± 0.4	–
HDPE + 20% WF	1116.7 ± 60.4	18.8 ± 0.7	6.3 ± 0.8
HDPE + 30% WF	1365.3 ± 122.5	17.8 ± 1.3	2.9 ± 0.5
HDPE + 40% WF	1490.2 ± 97.1	17.5 ± 0.9	2.1 ± 0.3

[a] WF, wood flour.

[b] According to supplier (ISO/DIS 6259, 50 mm/min).

engineering stress–strain curves of XLPE and HDPE plastics and composites thereof with 40% wood flour is shown. As can be seen in Fig. 6, the tensile strength for the crosslinked composite with 40% wood flour is much higher than for neat XLPE, while the tensile strength of non-crosslinked composite is lower than for neat HDPE. The elongation at break is also much higher for the crosslinked composite compared to the non-crosslinked. It is also interesting to compare the change in modulus with addition of wood flour for the crosslinked and non-crosslinked samples. The modulus increase for the crosslinked samples is 62% when comparing neat XLPE and a composite with 40% wood flour, while the same modulus increase for the non-crosslinked samples is 53%. This shows that the crosslinking also has an effect on the modulus and stiffens up the continuous plastic phase.

When comparing the mechanical data of the neat plastics according to the supplier in Table 1 and the measured data in Table 4, the values differ greatly. The values in Table 1 are over all higher than the measured data, even though the data for XLPE refer to non-crosslinked polyethylene. This is explained by the different test method used to measure the mechanical properties. The supplier data are measured with standardised test bars at a rate of 50 mm/min for tensile stress at yield and 1 mm/min for modulus of elasticity measurements. The measured data in Table 4 are measured with a miniature materials tester (Minimat) with rectangular test specimens at a rate of 3 mm/min. The mechanical data are not obtained using the same test method and are thus not comparable.

3.4.2. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analyses (DMTA) were carried out on various composites and neat plastics in tensile mode. Analysed samples were; neat XLPE and composites with 20%, 30%, 40% wood flour. In the system, there are two major transitions, corresponding to the HDPE γ-transition occurring at about −128 °C and then the α-transition at about 113 °C. Unplasticized HDPE does not display an apparent β-transition because its crystallinity greatly reduces the relaxation intensity [25]. The constraints imposed by the crystalline phase also broaden the β-transition, shifting it to higher temperatures, where it merges with the α-relaxation peak associated with the melting temperature [25]. According to Murayama as reported by Khonakdar et al. [26], the γ-transition of polyethylene is caused by motion in the amorphous regions of segments of chains comprising three or four CH_2 units.

The DMTA measurements can give knowledge about the interface between wood flour and polyethylene matrix. According to Nielsen as reported by Lai et al. [10], tan δ broadens and the peak position shifts if there is an interaction between the matrix polymer and the filler/reinforcement. In case of good adhesion between the wood and the matrix, one would expect a shift in the γ-transition towards higher temperature. In Fig. 7, tan δ versus temperature of the analysed samples is plotted. Fig. 8 shows a magnification of the area around the γ-transition. As can be seen in Fig. 8 and Table 5, there is no significant shift in γ-transition towards a higher temperature when wood flour is added to the plastic (XLPE). In addition, since the crosslinking is done in the solid state, the crystalline phase does not undergo any changes rather the crosslinking takes place only in the amorphous phase. This restricts molecular mobility of the polymer chains and hence shifts the γ-transition to higher temperature [26]. A further shift in the γ-transition towards higher temperatures would thus be expected for the composites compared to neat

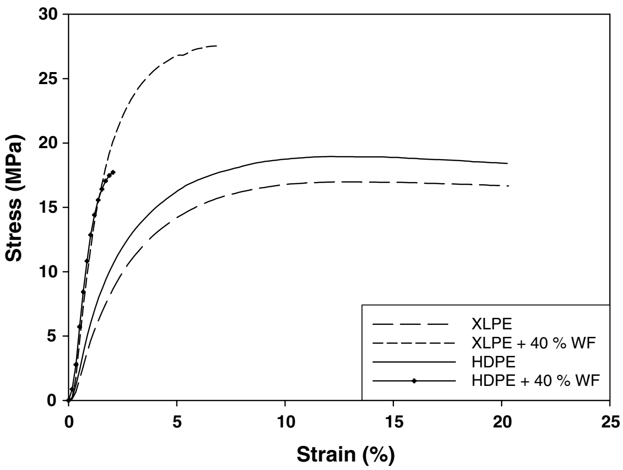


Fig. 6. Engineering stress–strain curves of crosslinked (XLPE) and non-crosslinked (HDPE) plastics and composites thereof with 40% wood flour.

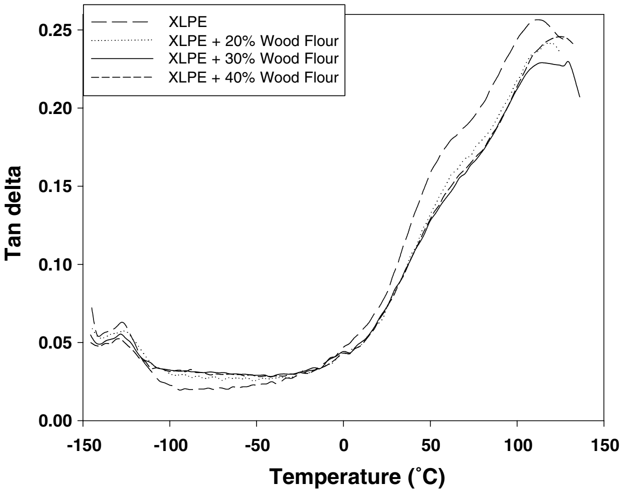


Fig. 7. Tan δ as a function of temperature for neat XLPE and composites with 20%, 30%, and 40% wood flour.

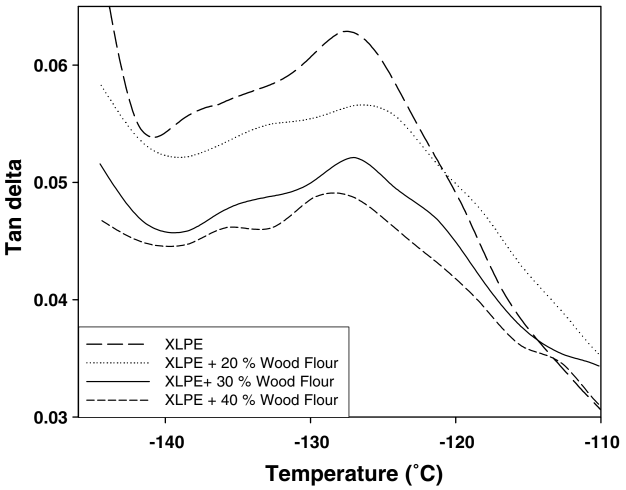


Fig. 8. Tan δ as a function of temperature for neat XLPE and composites with 20%, 30%, and 40% wood flour. Magnification of the area around the γ-transition.

Table 5
γ-Transition and α-transition of neat XLPE and composites with 20%, 30%, and 40% wood flour

Sample	γ-Transition (°C)	α-Transition (°C)
XLPE	−127.9	113.0
XLPE + 20% wood flour	−126.9	122.3
XLPE + 30% wood flour	−126.9	116.9
XLPE + 40% wood flour	−129.8	128.4

XLPE as a result of the higher degree of crosslinking in these samples. Moreover, there is a shift towards higher temperature of the α-transition for the composites compared to neat XLPE. This indicates that there is a partially hindered mobility of polyethylene chains in the crystalline phase, and it is influenced by the amount of wood flour. According to Balasuriya et al. [27], such a phenomenon was described as physical interaction between polyethylene (PE) and wood as possible nucleation of PE crystals at wood surfaces. However, an increase in crystallinity would reduce the molecular motions of the amorphous phase and thus lead to an increase in temperature of the γ-transition peak. Thus, there are several reasons to expect a shift in the γ-transition towards higher temperature for the composites, a phenomena which was not observed in the DMTA-analyses. One explanation to this phenomenon could be that the generated crosslinks are to few (low crosslink density) to cause a shift in the γ-transition peak. The bonding between the silanol groups and the wood could also be a combination of covalent bonds and hydrogen bonds. Hydrogen bonds are weaker than covalent bonds and thus more difficult to detect. Moreover, Lai et al. [10] studied composites of HDPE/wood flour where they used different maleic anhydride-grafted-polyethylene as compatibilizers. DMTA measurements of composites with 30% (w/w) wood flour were performed to study the γ-transition. A small shift in the γ-transition peak was observed when maleic anhydride (MA) grafted linear low density polyethylene (LLDPE) was used as compatibilizer. On the other hand, no shift in the γ-transition peak was observed in composites where MA-grafted-HDPE and MA-grafted-PP were used as

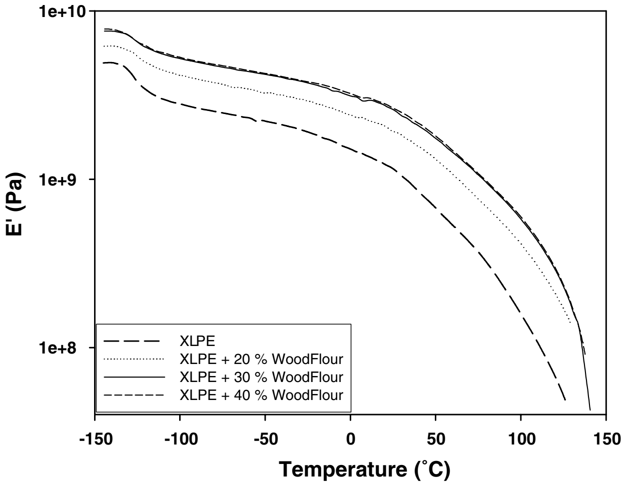


Fig. 9. Storage modulus as a function of temperature for neat XLPE and composites with 20%, 30%, and 40% wood flour.

Table 6
Storage modulus for the different samples at 25 °C

Sample	Storage modulus (MPa) at 25 °C
XLPE	1133.7
XLPE + 20% wood flour	1880.1
XLPE + 30% wood flour	2467.9
XLPE + 40% wood flour	2529.7

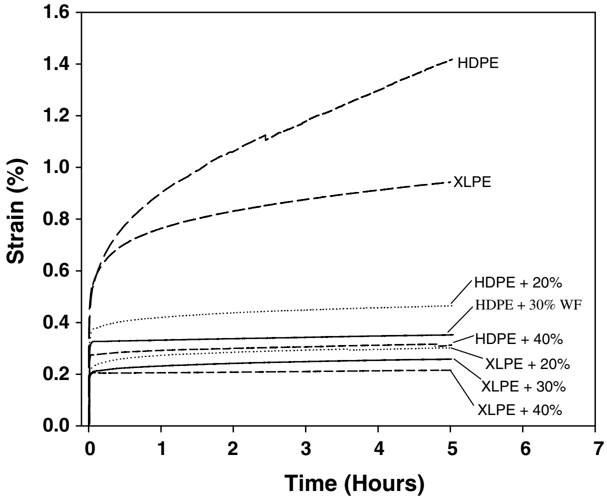


Fig. 10. Strain as a function of time during creep experiments at 30 °C for neat plastics and composites with different amounts of wood flour.

compatibilizers. The use of all the compatibilizers improved the tensile strength of the composites significantly, as a result of improved interfacial adhesion between the wood and the matrix. This shows that a shift in the γ-transition peak in composites with polyethylene as matrix might be difficult to observe, even in case of good adhesion.

The storage modulus (E') as a function of temperature for neat XLPE and composites with 20%, 30%, and 40% wood flour is shown in Fig. 9. The storage modulus at 25 °C for the different samples is summarised in Table 6. As can be seen in Table 6, the modulus is increasing with increased amount of wood flour. There is a 55% increase in modulus when comparing neat XLPE and the composite with 40% wood flour. This correlates rather well with the results from the tensile measurements which showed a 62% increase when the same comparison was made.

3.4.3. Short-term creep

Short-term creep experiments of composites and plastics were performed on the same DMTA instrument to

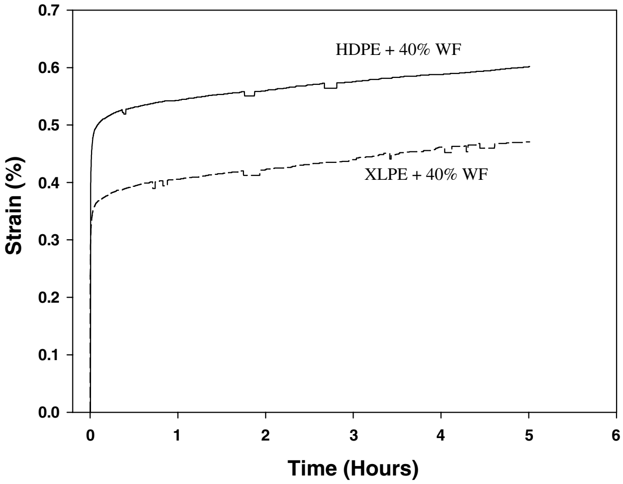


Fig. 11. Strain as a function of time during creep experiments at 60 °C for a crosslinked composite (XLPE) and a non-crosslinked (HDPE) with 40% wood flour.

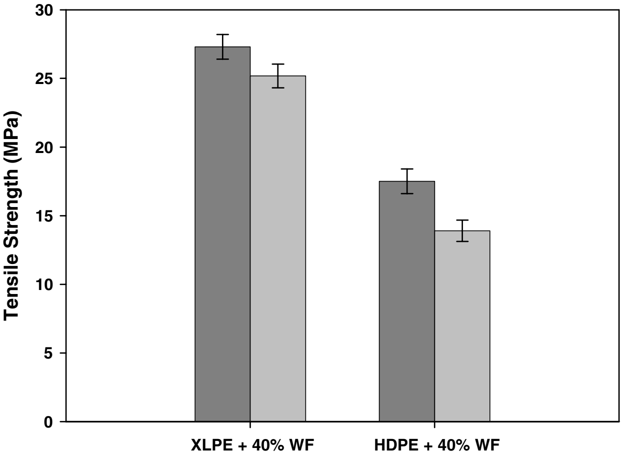


Fig. 12. Tensile strength before (dark grey bars) and after boiling test (light grey bars) of crosslinked (XLPE) and non-crosslinked (HDPE) composites.

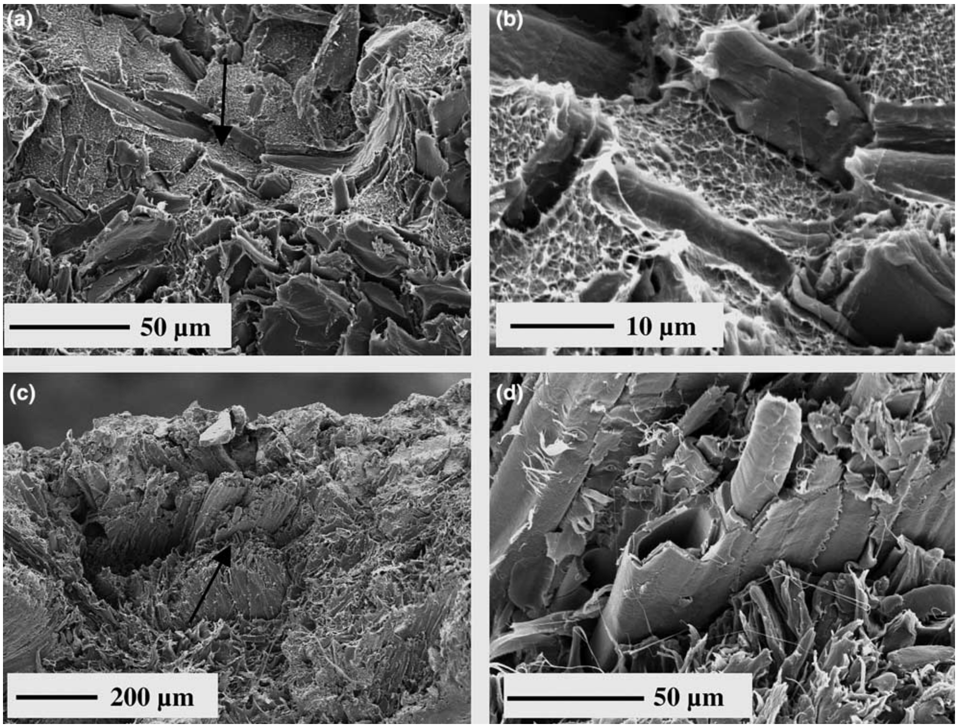


Fig. 13. SEM micrographs of the fracture surface of HDPE + 30% wood flour.

measure the deformation as a function of time at 30 and 60 °C. The duration of the experiments was 5 h and the applied static stress was 2 MPa in all the experiments. In Fig. 10, the creep strain as a function of time for neat plastics and composites (crosslinked XLPE and non-crosslinked HDPE) with different amounts of wood flour at 30 °C is shown. As can be seen in the figure, the neat plastics showed largest deformation in the range of time analysed. When wood flour was added the deformation decreased significantly and continued to decrease with increased amount of wood flour. All the crosslinked samples showed less deformation compared to the non-crosslinked ones. Crosslinking thus has a positive effect on reducing deformation during creep experiments. When the temperature was increased to 60 °C, the deformation response increased. In Fig. 11, the strain as a function of time for crosslinked (XLPE) and non-crosslinked (HDPE) composites with 40% wood flour at 60 °C is shown. It is evident from the figure that the deformation response is larger at higher temperature and also that the crosslinked composite is less affected. The small fluctuations in the measuring data are probably caused by a small variation in the temperature during the experiment. The reason for the reduction of deformation in the crosslinked composites compared to the non-crosslinked ones could both be related to a interlocking of the molecular chains in the matrix due to crosslinking and also due to an improved adhesion between the matrix and wood flour as a result of the crosslinking reaction.

3.4.4. Boiling test

A boiling test and subsequent tensile testing was performed to evaluate the interfacial adhesion between the wood and the polymer matrix. In case of good adhesion, the strength loss of the composites would not be as sig-

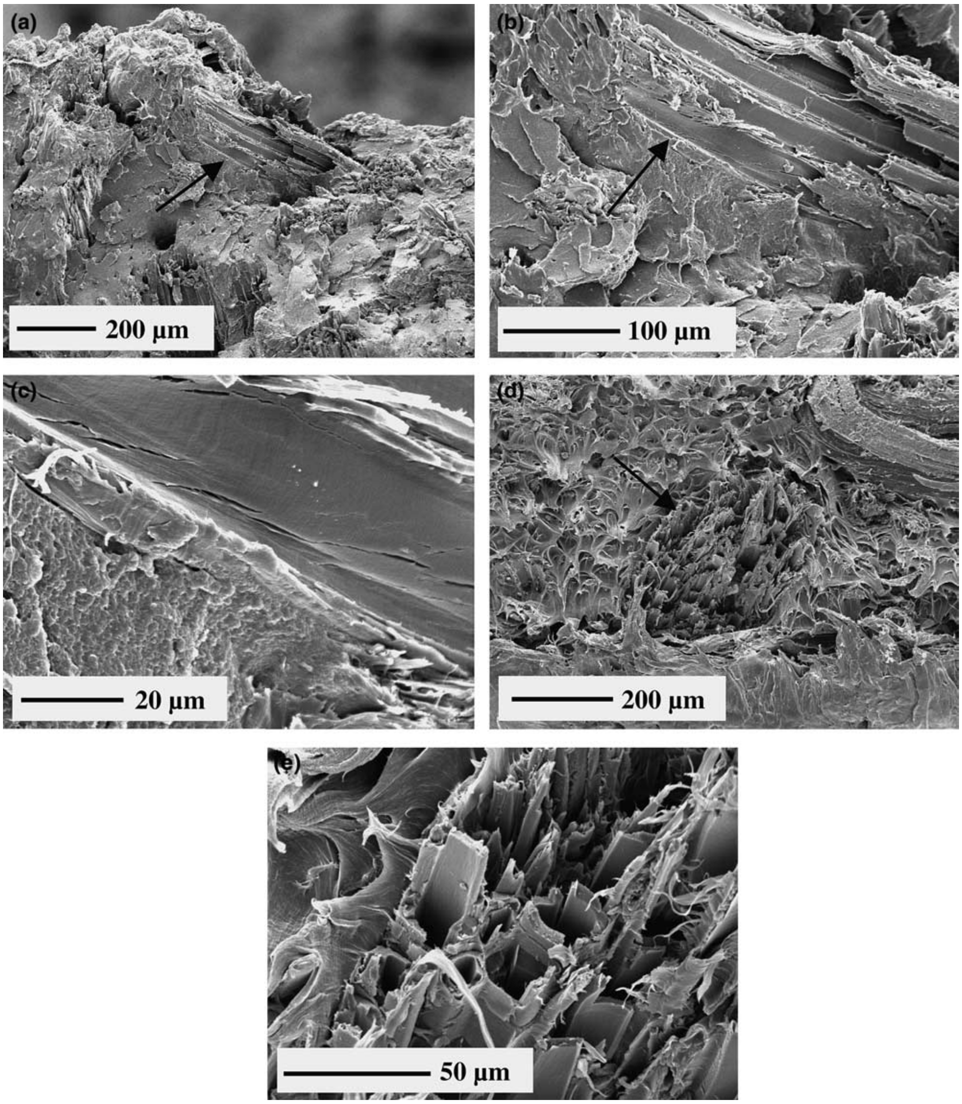


Fig. 14. SEM micrographs of the fracture surface of a crosslinked composite with 30% wood flour. The gel content of this sample was 50%.

nificant as if adhesion is lacking. Analysed samples were composites with 40% wood flour, both crosslinked with XLPE as continuous phase and non-crosslinked with HDPE as continuous phase. After boiling the average water content of the crosslinked and non-crosslinked composites was 5.9% and 10.3%, respectively. A higher water content is an indication of poor encapsulation of the wood flour by the polymer matrix which acts as a barrier to water penetration to the system. In Fig. 12, the tensile strength of the samples before the boiling test is compared with the strength after boiling and reconditioning to a water content less than 0.5%. As can be seen in the figure, the tensile strength after boiling is decreasing for both the crosslinked and non-crosslinked composites. However, the loss in tensile strength for the non-crosslinked is more significant (−20.6%) compared to −7.8% for the crosslinked composite. The improved water resistance in the crosslinked sample could be related to a better bonding between the wood flour and the polymer matrix. Other possible explanations for the reduction in water penetration could be related to the permeability of the neat polyethylene matrix. However, density measurements of the neat polyethylene materials showed a density of 946 and 940 $\mathrm{kg/m^3}$ for HDPE and XLPE, respectively. The density of the non-crosslinked matrix was thus higher than for the crosslinked one and should thus be less susceptible for water absorption. This shows that the reason for improved water resistance in the crosslinked composite is most likely interfacial.

3.5. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to monitor the fracture surface of the composites after quenching the samples in liquid nitrogen. In Figs. 13 and 14, respectively, the fracture surfaces of non-crosslinked and crosslinked composites are shown. In the non-crosslinked composite with HDPE as matrix (Fig. 13(a)–(d)), there are distinct gaps between the matrix and the wood, indicating poor adhesion. In Fig. 13(a)–(b), it is also possible to observe patterns from wood fibres which were so weakly bonded to the matrix that they have been released from the matrix during fracture. Fig. 13(d) also shows that part of the wood lumen is filled with plastic which could increase the strength of the composites as a result of mechanical interlocking.

Fig. 14(a)–(e) is showing the fracture surface of a crosslinked composite with XLPE as matrix filled with 30% wood flour. Fig. 14(a)–(c) shows that there are no gap between the plastic and the wood surface, indicating good adhesion. In Fig. 14(c), it is also possible to observe a crack running through the wood fibre. This could be an indication of stress-transfer from the weaker matrix to the stronger wood fibre which only is possible in case of good adhesion between the phases. Fig. 14(d)–(e) shows that the lumen of the wood fibres is not filled with plastic. The melt index of XLPE is higher than for HDPE which could explain that the lumen is not filled with plastic.

4. Conclusions

Crosslinked composites of vinyltrimethoxy silane-grafted-HDPE and wood flour were produced by compounding in a co-rotating twin-screw extruder. The gel content in the crosslinked composites was higher compared to crosslinked matrix, as determined by *p*-xylene extraction. A higher gel content in the composites compared to neat matrix could be explained by the hygroscopic nature of wood leading to a higher water content in the composites and thus an acceleration in the water dependent crosslinking. Tensile testing of the samples showed an increase in stiffness with increasing amount of wood flour and an accompanied decrease in strain at failure. More, interesting was the significant increase in tensile strength with increasing amount of wood flour. Such phenomena were not observed in the composites where a non-crosslinkable matrix was used and is an indication of interaction between wood and polymer in the crosslinked composites. The elongation at break was also much higher for the crosslinked composite compared to the non-crosslinked. Dynamic mechanical thermal analysis (DMTA) showed no significant shift in the γ-transition peak position towards higher temperature when crosslinked samples of neat plastic and composites were compared. A low crosslink density is believed to be the reason for the absence of a shift in the γ-transition peak. Short-term creep experiments showed reduced deformation with increasing amount of wood flour. Crosslinking of the composites also reduced the amount of deformation during the creep experiments. A boiling test in water followed by tensile testing showed that the crosslinked composites were less susceptible to water uptake compared to the non-crosslinked. Moreover, the decrease in tensile strength of the crosslinked samples was not as significant as for the non-crosslinked composites. Scanning electron microscopy was used to monitor the fracture surfaces of crosslinked composites of vinyltrimethoxy silane-grafted-polyethylene/wood flour and non-crosslinked composites of polyethylene/wood flour. The crosslinked composites showed good compatibility and adhesion between the plastic and the wood flour, while the non-crosslinked composites showed poor adhesion between the two phases.

This study is to be followed by a more throughout investigation where the effect of different degree of silane grafting of polyethylene and various levels of crosslinking is affecting the properties of composites made thereof.

Acknowledgements

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Paper II

The use of silane technology in crosslinking polyethylene/wood flour composites

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The use of silane technology in crosslinking polyethylene/wood flour composites

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Abstract

In this study, the use of silane technology in crosslinking polyethylene–wood flour composites have been investigated. Composites were produced in a one-step process using a co-rotating twin-screw extruder. The composites were stored in a sauna and at room temperature to study the effect of humidity on the degree of crosslinking. Crosslinked composites showed improved toughness and creep properties compared to non-crosslinked composites. The flexural modulus, on the other hand, was lower in the crosslinked samples than in the non-crosslinked ones. FTIR was used to study the crosslinking reaction in the samples. X-ray mapping of the silicon signal was also performed to locate the silane in the composites. This study provides a basis for proposing, that part of the silane is grafted onto polyethylene and wood thereby creating a crosslinked network in the matrix with chemical bonds (covalent and hydrogen bonding) to wood. The other part of the silane remains un-reacted and blends into the system.

Keywords: A. Polymer-matrix composites (PMCs); B. Fibre-matrix bond; E. Extrusion; Crosslinking

1. Introduction

Natural- and wood fibre plastic composites (WPC) have gained significant popularity in the last decade. The retail value of this industry has been growing nearly 16% annually since 1998, and is currently valued at over $750 millions [1]. These relatively new composite materials are used to replace impregnated wood in exterior applications. One of the reasons for the growing interest in WPC is the recent concern about the preservatives used in the wood impregnation. Chromated copper arsenate (CCA) is currently the most widely used wood preservative due to its excellent fungicidal and insecticidal properties [2]. However, the impact this and other chemicals may have on the environment is cause for concern. In the US, this has resulted in a phase-out of all new uses of CCA impregnated wood for residential purposes. Another reason for replacing the use of impregnated wood is that the impregnation treatments do little to hinder the dimensional changes that accompany moisture absorption [1]. WPC also has advantages over pure plastics. The elastic modulus of wood fibre is approximately 40 times higher than that of polyethylene and the strength about 20 times higher [3]. When added to plastics, wood increases stiffness, an advantage in certain areas of use. When proper coupling agents are used to improve fibre-matrix adhesion, wood can also be used to reinforce the plastic. There are also economical and environmental reasons for replacing part of the plastic with wood fibre.

The increased interest in the use of wood as filler and/or reinforcement in plastics is due to the many advantages. Low density, high stiffness and strength, and low price are some of these advantages [4–7]. Processing of wood composites minimises abrasion of equipment due to the low hardness of wood compared to the inorganic fillers previously used to a great extent [5]. Moreover, wood is not only aesthetically pleasing but also renewable, recyclable and biodegradable [8]. In spite of all the advantages mentioned above there are also drawbacks in using wood fillers as reinforcement in thermoplastics. The main drawbacks are the difficulties of achieving good dispersion and strong interfacial adhesion between the hydrophilic wood and the hydrophobic polymer. Poor adhesion leads to composites with rather poor durability and toughness [5,6,9–11].

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During the past two decades several different methods have been tested in order to improve the adhesion between the wood filler and the thermoplastic matrices. Among the most common used coupling agent is maleated polyethylene or polypropylene [5,10–14]. There have also been some studies on other coupling agents such as isocyanates [9,15] and silanes [9,15,16]. In general, the use of these coupling agents significantly improves the mechanical properties of the composites.

Wolcott and Smith [1] claimed that WPCs are sufficiently strong to resist the loads expected in many structural applications but improvements are necessary in both long-term load performance and product weight. Foaming or use of hollow or shaped cross sections can be used to reduce the weight of WPCs [1]. Adding wood filler to the plastic matrix decreases the creep response during loading [17,18], but does not completely alleviate the problem. Crosslinking of the polymer matrix might be one way of reducing the creep during long-term loading. Several techniques have been developed to obtain crosslinked polyethylene: peroxide crosslinking, irradiation techniques and silane crosslinking. However, both peroxide and irradiation crosslinking techniques involve high investment costs [19]. Other drawbacks are the risk of pre-curing and high production cost during peroxide crosslinking and the thickness limitation in radiation crosslinking [19]. The silane crosslinking 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 crosslinked after the processing steps. Crosslinkable ethylene-vinyl silane copolymers are a commercial product for the global wire and cable market. Vinyl silanes can be grafted onto the polyethylene backbone by the use of small amount of peroxide or co-polymerised with ethylene in the polymerisation reactor. The grafting of vinyl silanes onto the polyethylene backbone can be made more efficient by the use of platinum based catalysts [20,21]. The silane crosslinking takes place in the presence of trace amounts of water and the reactions can be accelerated by incorporating a tin-based catalyst. The silane crosslinking reaction proceeds over two steps. In the first step the methoxyl groups are hydrolysed to hydroxyl groups during leaving of methanol. The crosslinking takes place in the second step where the hydroxyl groups recombine through a condensation step [22], as shown in Fig. 1. In an earlier study with silane grafted HDPE, it was shown that wood could be incorporated in the crosslinked network since the silanol groups created in step 1 could react with hydroxyl groups in wood as well as with other hydroxyl groups grafted on the polyethylene backbone [18]. It was shown that the creep response during short-term loading was decreased upon silane crosslinking of the composites. Moreover, the toughness of the silane crosslinked composites was significantly higher than for non-crosslinked ones. Kuan et al. [23] studied silane crosslinked linear-low density polyethylene–wood flour composites. The wood flour was treated with vinyltrimethoxy silane (VTMS) before compounding with polyethylene. The crosslinking was subsequently initiated by water treatment. Water crosslinked samples exhibited better mechanical properties than the non-crosslinked ones and this was explained as a result of chemical bonding between both wood and polyethylene. Other studies have used peroxides to crosslink composites of polyethylene and wood flour/pulp [24,25]. The mechanical properties of the crosslinked composites were better than the non-crosslinked. It was shown that crosslinking improved the adhesion between the polyethylene and the wood filler as a result of recombination of radicals formed at the filler surface and polyethylene macro radicals.

In this study, the silane grafting and composite production were carried out simultaneously in a one-step

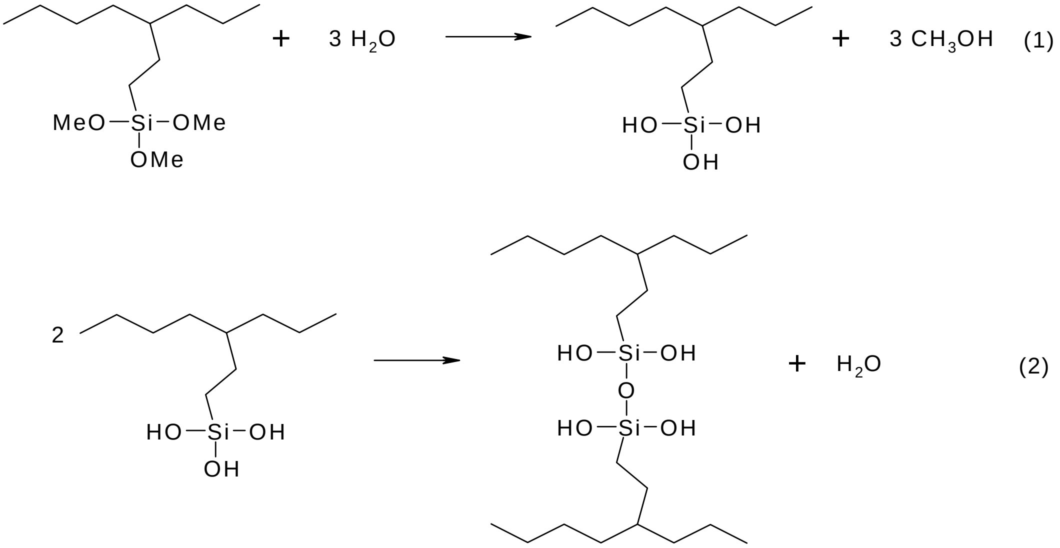

Fig. 1. The hydrolysis step (1) and condensation step (2) during silane crosslinking.

process. By doing so, the production of the composites is more economical and also believed to be more industrially friendly. Moreover, by doing the composite manufacturing and silane grafting ourselves, we achieve better control over the degree of crosslinking in the composites. This article is based on an earlier article by the same authors within the same topic area [18].

2. Experimental

2.1. Materials

High density polyethylene, HDPE MG9601 (MFI = 31 g/10 min, 190°C/5 kg), was purchased from Borealis AB (Stenungsund, Sweden). Wood flour from softwood (spruce and pine) was kindly provided by Scandinavian Wood Fiber AB (Orsa, Sweden). According to the supplier the size of the softwood wood flour was 200–400 μm. The shape of the wood flour was fractured fibre bundles. VTMS 98% was purchased from Sigma Aldrich (Leirdal, Norway). Dicumyl peroxide, Perkadox BC-FF, was kindly supplied by Akzo Nobel (Gothenburg, Sweden). In this paper, the crosslinked samples are sometimes referred to as “XLPE” and the non-crosslinked samples as “HDPE”. Samples stored at room temperature (24 days) and in a sauna (24 h) are abbreviated RT and SA, respectively.

2.2. Processing

The wood flour was dried for 24 h at 100°C to a moisture content of ~1% (based on dry weight) before processing. Plastic granulates and wood flour were compounded using a Coperion Werner and Pfleiderer ZSK 25 WLE (Stuttgart, Germany) corotating twin-screw extruder. As can be seen in Fig. 2, the barrel temperatures were between 175 and 200°C, the screw speed was 150 rpm, the pressure at the die varied between 8 and 35 bars depending on material blend, and the material output was 5 kg/h during extrusion. Polyethylene and wood flour was gravimetrically fed to the extruder. Feeding of the wood flour was performed at temperature zone 4 through a twin-screw side feeder operating at 150 rpm. Silane crosslinked specimens were produced by pumping a solution (8.2 g/min) of VTMS and dicumyl peroxide (10:1 w/w) into the extruder at temperature zone 1. Vacuum ventilation at the end of the extruder was used to minimise volatile extractives and un-reacted silane in the final composites. The composites were produced in a one-step process and the compounds were extruded through a rectangular die with the dimensions of 5×30 mm and cooled in ambient. After extrusion the composites were ground into standard test specimens for mechanical testing. The neat plastics were granulated in a rotating knife mill. The plastic granulates were then injection moulded into ASTM standard specimens for mechanical testing on a Cincinnati Act. Milacron 50 machine (Cincinnati, OH, USA). Machine settings: 190°C first zone, 200°C zone two to four, injection pressure 1500 bar, injection velocity 100 mm/s, packing pressure 500 bar (10 s), cool time 20 s. The material formulations are shown in Table 1.

2.3. Silane crosslinking

After processing, the specimens were stored at different environments to study the effect of humidity on the degree of crosslinking. The storage environments were a simulated sauna at approximately 100% RH and 90°C and at room temperature with temperature between 21 and 26°C and humidity between 28 and 43%. The sauna-stored samples were subsequently dried to their initial weight before testing.

2.4. Gel content

The gel content of the samples was determined using p-xylene extraction according to ASTM standard 2765. The specimens to be analysed were ground and placed in folded 120 mesh stainless steel cloth cages. Cages with ground sample were weighed before immersion in p-xylene. Butylated hydroxytoluene (BHT) was used as an antioxidant to inhibit further crosslinking of the specimen and 1% of BHT was dissolved in 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 different blends was determined as the average of two separate

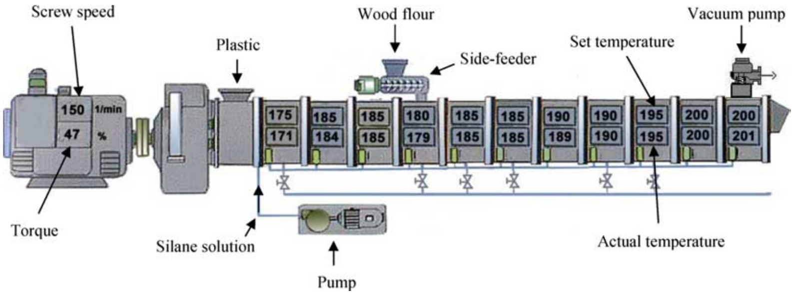

Fig. 2. Extruder setup during processing.

Table 1
Formulations of produced materials

		Weight (%)		
Sample code	Storage	HDPE MG9601	Wood flour	Chemically bonded VTMS[a]
XLPE-RT	RT[b]	97.4	–	2.6
XLPE29-RT	RT	68.0	29.2	2.8
XLPE39-RT	RT	58.6	39.0	2.4
XLPE44-RT	RT	53.8	44.0	2.2
XLPE-SA	SA[c]	97.4	–	2.6
XLPE29-SA	SA	68.0	29.1	2.9
XLPE39-SA	SA	58.5	39.0	2.5
XLPE44-SA	SA	53.8	44.0	2.2
HDPE-RT	RT	100.0	–	–
HDPE30-RT	RT	70.0	30.0	–
HDPE40-RT	RT	60.0	40.0	–
HDPE45-RT	RT	55.0	45.0	–

[a] In addition, there might also be un-reacted vinyltrimethoxy silane (VTMS) in the samples.
[b] RT = Stored in room temperature for 24 days.
[c] SA = Stored in a simulated sauna for 24 h.

analyses. The gel content was calculated according to the following equation:

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

$$\text{Gel content} = 100 - \text{Extract}\% \tag{1}$$

2.5. Amount of chemically bonded silane

The amount of chemically bonded silane in the samples was determined from a combustion experiment in an air oven at 600°C for 5 h. The samples were first soxhlet extracted for 6 h at 150°C with p-xylene to remove unreacted silane from the samples, dried and then weighed before and after combustion. The ash content after combustion was assigned to silicon dioxide (SiO_2). To confirm that the ash was silicon dioxide, it was analysed with FTIR (see Section 2.8). The amount of $–(CH_2)_2–Si–(OH)_3$ in the samples before combustion could then be calculated back from the amount of silicon dioxide in the ash. Since wood contains small amounts ($>0.1\%$) of silicon naturally, composites to which no silane was added were used as reference. The ash content in the reference samples was subtracted from the samples to determine the correct amount of chemically bonded silane. At least five specimens from each blend were tested.

2.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) tests were performed on a DSC-7 (Perkin Elmer, Germany) with samples of approximately 10 mg sealed in aluminium pans. The samples were analysed under nitrogen atmosphere in a temperature range between 25 and 170°C at a heating range of 10°C/min. The melting temperature and enthalpy of fusion of the samples were determined. All samples were run in duplicates.

2.7. Mechanical testing

2.7.1. Flexural properties

Flexural properties of the samples were measured on an Instron-Schenk 8800 instrument (High Wycombe, Great Britain) in accordance with ASTM D790. The dimensions of the specimens tested were approximately 3.2×12.7×130 mm. The measurements were performed at ambient conditions, i.e. a temperature of 22°C and a relative humidity of approximately 40%. At least five specimens of each blend were tested.

2.7.2. Impact strength

Izod impact strength of un-notched composite specimens was tested on an Otto Wolpert-Werke (Ludwigshafen, Germany) instrument in accordance with ASTM D256-97. The dimensions of the specimens tested were approximately 3.2×12.7×50 mm. The measurements were performed at ambient conditions, i.e. a temperature of 22°C and a relative humidity of approximately 40%. The impact energy was divided by the width of the specimens to yield impact strength (J/m). At least five specimens of each blend were tested.

2.7.3. Creep properties

For the most general case of a linear viscoelastic material the total strain e is the sum of three essentially separate parts: e_1 the immediate elastic deformation, e_2 the delayed elastic deformation and e_3 the Newtonian flow, which is identical with the deformation of a viscous liquid obeying Newton's law of viscosity [26]. The magnitudes of e_1, e_2 and e_3 are exactly proportional to the magnitude of the applied stress, so that a creep compliance $J(t)$ can be defined, which is the function of time only:

$$J(t) = \frac{e(t)}{\sigma} = J_1 + J_2 + J_3 \tag{2}$$

where J_1, J_2 and J_3 correspond to e_1, e_2 and e_3 [26]. Crosslinked polymers do not show a J_3 term, and to a very good approximation neither do highly crystalline polymers.

Short-term creep experiments of composites were performed using a Rheometrics Dynamic Mechanical Thermal Analyser DMTA V (Rheometric Scientific, Piscataway, NJ, USA). The measurements were performed in dual cantilever mode on specimens measuring approximately 1.6×12×30 mm. The applied static stress was fixed at 5 MPa and the temperature was fixed at 30°C.

Creep cycling test was performed on the same instrument with the same sample dimensions and test mode. A 2 MPa stress was applied on the samples at 60°C for 1 h and then released for 1 h and then applied again. This procedure was repeated three times.

2.8. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was used to study the crosslinking reaction in the composites, i.e. the formation of wood–O–Si bonds and Si–O–Si bonds. FTIR was also used to analyse the ash after the combustion experiment. FTIR was measured (4000–600 cm^{-1}) with a UMA-250 FT-IR (Bio-Rad Laboratories Inc., Cambridge, MA, USA). The samples to be analysed were cooled in liquid nitrogen and then ground to a fine powder. This powder was then mixed with KBr at a weight ratio of 3/150 mg and subsequently pressed at 10 metric tons to form a tablet. The average of 50 spectra was used to increase the signal to noise ratio.

2.9. Electron probe microanalyser (EPMA)

X-ray microanalysis of the composites was performed on an electron microprobe JXA-8900 Superprobe (JEOL, Tokyo, Japan). This microprobe is basically a scanning electron microscope designed and optimised for x-ray analysis of elements from very small areas. Backscatter electrons were used to collect images of the samples. These images were then used to select areas where x-ray mapping of the silicon-signal was performed. The mapping was performed with the aim of trying to find where the silane was located in the composites. Four wavelength dispersive x-ray spectrometers (WDS) were used during the analysis and the acceleration voltage and beam-current were 10 keV and 15 nA, respectively. The samples were embedded in an epoxy matrix and diamond polished to 0.25 μm. To avoid charge build-up, the samples were coated with a thin layer of carbon.

3. Results and Discussion

3.1. Silane grafting

During the processing of crosslinked composites and plastics, a solution of VTMS and peroxide was pumped into the extruder during processing. At elevated temperature the peroxide first decomposes and creates oxy radicals. These oxy radicals not only have the potential to abstract hydrogen from the polyethylene- or wood polymer but can also attack the vinyl group of the VTMS molecule and convert it into radicals. These free radicals either combine with one another or attack another molecule in the same fashion to propagate the free-radical reaction [27]. This process results in grafting of vinyl silane onto polyethylene or wood chains; this is a prerequisite for crosslinking the material. Fig. 3a shows the reaction mechanism during peroxide-induced melt grafting of silane onto polyethylene. The opportunity of grafting VTMS on both HDPE and wood flour is thus present. Moreover, there is a possibility of a direct condensation reaction between silanol groups (Si–OH) and hydroxyl groups on wood. This would create a covalent bonding between wood and the silanol group (wood–O–Si), where the hydrophobic part of VTMS (vinyl group) could be chemically bonded (covalent C–C) or interact through van-der-Waals forces with the polyethylene matrix. Melt phase processing of polyolefins is often accompanied by side reactions. These include [28]:

(a) radical-induced crosslinking of the polyolefin
(b) radical-induced chain scission of the polyolefin
(c) shear-induced degradation of the polyolefin
(d) homo-polymerisation of the monomer

Polyethylenes (HDPE, LDPE, LLDPE) are prone to branching or crosslinking caused by radical–radical combination [28]. Fig. 3(b) shows the reaction mechanism caused by radical induced crosslinking of polyethylene. There is thus a possibility that some of the crosslinked network in the specimens is caused by a radical–radical combination. Radical induced chain scission and shear induced degradation is not as prominent for HDPE as it is for polypropylene (PP) [28]. In addition, vinylsilanes (e.g. VTMS) do not readily homo-polymerise [28].

3.2. Gel content

Storage at environments with different humidity levels, i.e. a simulated sauna at 90°C, ∼100% RH and at room temperature 21–26°C, 28–43% RH, affected the degree of

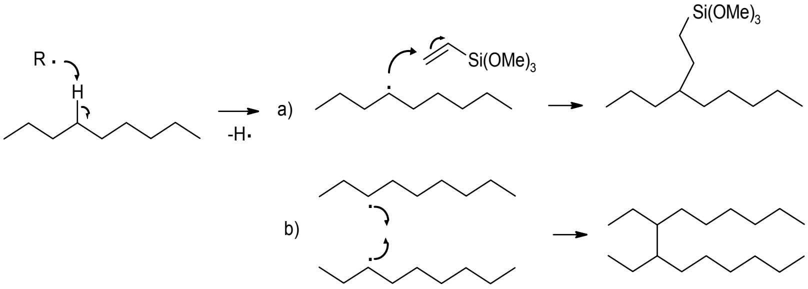

Fig. 3. The reaction mechanism during (a) peroxide induced melt grafting of silane onto polyethylene, (b) radical induced crosslinking of polyethylene.

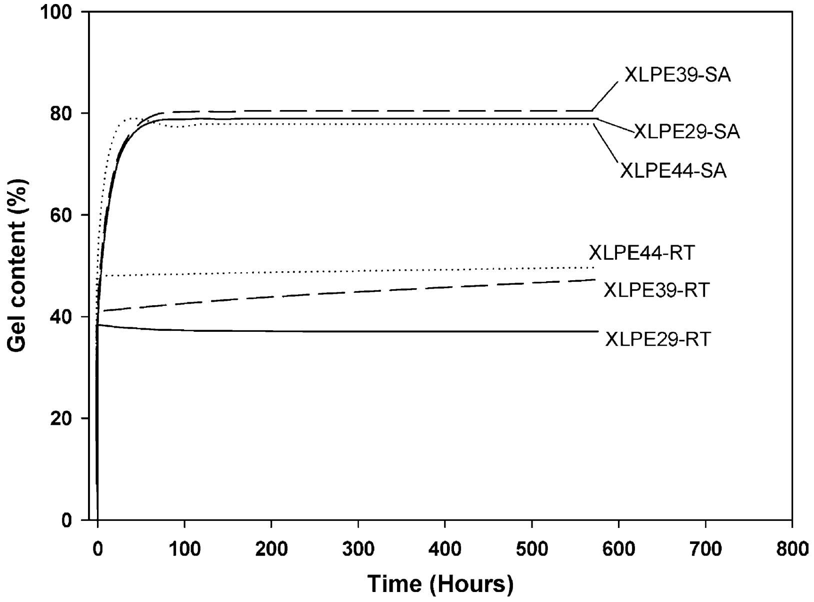

Fig. 4. Gel content as a function of storage time for composites with 29, 39 and 44% wood flour. The different storage environments were in sauna at 90°C, 100% RH and at room temperature.

crosslinking in the samples. As can be seen in Fig. 1, the first step in the silane crosslinking reaction is hydrolysis of the methoxyl groups to silanol groups. Water is responsible for the hydrolysis of the methoxyl groups. A higher humidity level would thus be expected to create a higher degree of crosslinking in the samples. As can be seen in Fig. 4, storage in a high humidity sauna generated a higher degree of crosslinking in the composites than storage at room temperature. The curves in Fig. 4 are fitted from the data in Table 2. Already after 24 h in the sauna, the gel content in all the composites was above 70%. A maximum gel content of approximately 80% was found after storage between 24 and 72 h in the sauna. The composite with 44% wood flour reach the maximum gel content already after 24 h in the sauna while the composites with 29 and 39% wood flour reach the maximum gel content between 24 and 72 h. The different amount of wood flour in the composites stored in the sauna did not seem to significantly influence the final gel content. Storage at room temperature slightly increased the gel content of the composite with 39% wood flour, but for the composites with 29 and 44% wood flour the gel content was more or less constant throughout time. This indicates that storage at room temperature does not provide the right environment for a significant increase in the degree of crosslinking of the composites. It is also interesting to note that the crosslinking is initiated already during the extrusion, represented by time zero in Fig. 4. This initial crosslinking can be due to silane crosslinking but might also be due to side reactions as was discussed in Section 3.1. At time zero a higher degree of crosslinking was found with increased amount of wood flour in the composites. As can be seen in Table 2, the gel content of neat XLPE is significantly lower than in the composites. The moisture in wood thus seems to play an important role in catalysing the silane crosslinking reaction. This phenomenon was already found during our first study of crosslinked composites with the use of silane technology [18].

3.3. Amount of chemically bonded silane

After combustion of the samples at 600°C, the ash was analysed with FTIR to confirm it was pure silicon dioxide (SiO_2). The obtained spectrum is shown in Fig. 5. As can be seen in the spectrum peaks corresponding to Si–O–Si, symmetric and asymmetric bending are located at 804 and 1109 cm^{-1} [29]. The small wider band at 3000–3800 cm^{-1} was attributed to hydroxyl groups; probably origin from water absorption during sample preparation for the FTIR analysis. The spectrum was also compared

Table 2
Gel content of neat XLPE and composites with XLPE as continuous phase

Storage Time (h)	Storage condition	Wood content (Weight (%)) 0	29	39	44
0	–	–	38	41	48
24	RT	22	37	41	47
72	RT	–	38	40	46
120	RT	–	38	43	47
168	RT	–	36	47	48
240	RT	–	37	47	48
576	RT	–	37	51	52
24	Sauna	64	71	72	79
72	Sauna	–	78	77	77
120	Sauna	–	83	78	80
168	Sauna	–	77	81	77
240	Sauna	–	77	81	78
576	Sauna	–	79	80	79

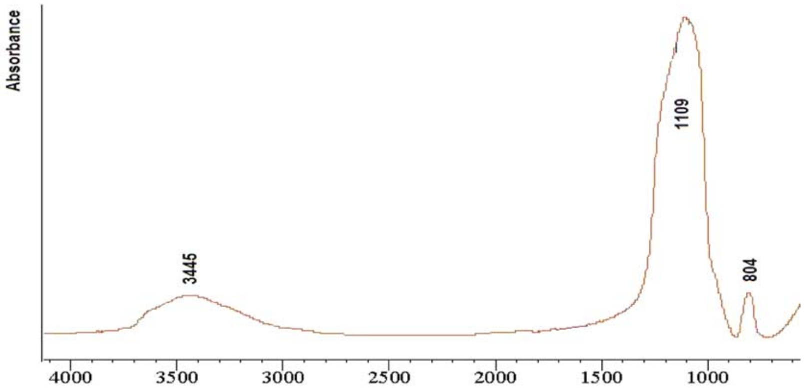

Fig. 5. FTIR spectrum of the ash after combustion of the samples at 600°C.

with an FTIR spectrum of pure silicon dioxide in a study of Hernandez-Padron et al. [29]. The two spectra proved to be equivalent and thus confirmed the purity of the silicon dioxide. The amount of chemically bonded silane in the samples is shown in Table 1. The amount of chemically bonded silane was highest in the composite with 29% wood flour (~2.8-2.9% w/w) and then decreased slightly when the proportion of wood flour was increased. This could be an indication that the silane has a slighter higher tendency to chemically react with the plastic than with the wood. On the other hand, the amount of chemically bonded silane in the neat plastic was lower than in the composite with 29% wood flour. This could be due to some silane reacting with wood through a direct condensation reaction between hydrolysed silane and hydroxyl groups in wood. Even though the amount of chemically reacted silane in the samples varies slightly it does not seem to influence the gel content in the samples (see Table 2). This shows that the amount of grafted silane in the composites is enough to fully crosslink the composites. A higher degree of silane grafting may have an effect on the crosslink density of the created network. Hjertberg, et al. [22] showed that the formation of Si–O–Si linkages, i.e. crosslinking points continued long after the maximum gel content was reached. This was explained as a result of molecules already part of the network forming even more crosslinks. Moreover, it is also important to note that besides the reacted silane there might also be un-reacted silane in the samples that has simply been blended into the materials.

3.4. Differential scanning calorimetry

Fig. 6 shows the DSC thermographs of neat HDPE and XLPE. As can be seen in the figure, the melting endotherm (ΔH_{fusion}) is lower in the crosslinked samples compared to the non-crosslinked ones. This is evidence of a lower degree of crystallinity in the crosslinked samples. The crystallinity in the samples was calculated according to the following equation:

$$\text{Crystallinity (\%)} = \frac{\Delta H_{\text{fusion, sample}}(\text{J/g})}{\Delta H_{\text{fusion, 100\% crystalline polyethylene}}(\text{J/g})} \tag{3}$$

An enthalpy of fusion of 290 J/g for 100% crystalline polyethylene was used in the calculation of crystallinity [30]. The melting peak temperature of the crosslinked samples was also slightly lower in the crosslinked samples than in the non-crosslinked. In Table 3 the crystallinity, melting endotherms (ΔH_{fusion}), and the melting peak temperatures from the DSC analysis are summarised. The slightly higher crystallinity in XLPE-SA compared to XLPE-RT could be related to some re-crystallisation taking place during storage in a sauna at 90°C. Since silane crosslinking mainly takes place in the solid state, the crystalline phase should not undergo considerable changes, rather the crosslinking takes place only in the amorphous phase. However, as was shown in Table 2 (gel content) the crosslinking reaction is initiated already during extrusion.

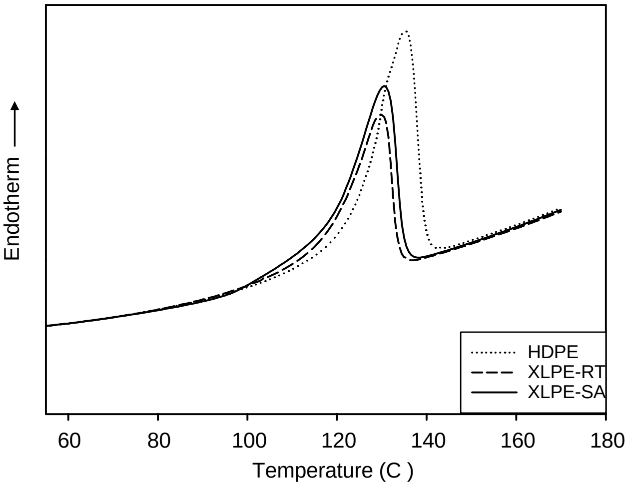

Fig. 6. DSC heating thermographs of neat HDPE and XLPE.

Table 3
Peak melting temperatures (T_m) and melting endotherms (ΔH_{fusion}) of neat plastics

Sample code	T_M (°C)	ΔH_{fusion} (J/g)	Crystallinity (%)
XLPE-RT	128.3	126.8	44
XLPE-SA	128.7	133.0	46
HDPE-RT	133.8	159.6	55

This initial crosslinking can be due to silane crosslinking but might also be due to side reactions as was discussed in Section 3.1. The crosslinked polyethylene forms a network structure. The network structure makes the macromolecules chain less flexible, so the crystallisation melt peak becomes lower and crystallisation more difficult. A lower crystallinity in silane crosslinked specimens has also been reported by other authors [30,31].

3.5. Mechanical properties

3.5.1. Flexural properties

In Fig. 7, the average values of the flexural strength as a function of wood flour content are shown. As can be seen in the figure, the flexural strength of neat HDPE was higher than in the XLPE samples. DSC-analysis showed a lower crystallinity of the neat XLPE samples than in neat HDPE. The lower crystallinity in the crosslinked samples could be one explanation for their lower strength. Another explanation for the lower flexural strength of the crosslinked samples in our study could be due to un-reacted silane. The amount of added silane was 9% w/w during extrusion and the amount of chemically bonded silane was determined to be less than 3% w/w. It is thus expected that some of the silane is just blended into the system without reacting. Part of the silane evaporated and/or ventilated out of the system during processing. The excessive amount of un-reacted silane could act as a plasticizer and lower the strength of the neat XLPE samples compared to neat HDPE. In contrast to the neat plastics, the crosslinked composites showed flexural strength superior to those composites to which no silane was added. There was a significant increase in flexural strength for the crosslinked samples when the wood flour content was increased from zero to 39%. The increase in strength with an increase in wood flour content is most likely caused by improved adhesion between wood and polyethylene. So even though the crystallinity of the polyethylene matrix was lower in the crosslinked samples than in the non-crosslinked, and there might be un-reacted silane plasticising the composites, the flexural strength was significantly higher in the crosslinked composites than in the non-crosslinked composites. Improved adhesion between wood and plastic makes it possible for stress transfer from the weaker plastic matrix to the stronger wood fibre during loading, thereby improving the strength of the crosslinked composites. The improved adhesion could be due to covalent bonding between wood and polyethylene through either condensation or free-radical reaction. Moreover, hydrogen bonding between silanol groups grafted on polyethylene and hydroxyl groups on wood, and van-der-Waals forces between condensated silane on wood and the polyethylene matrix, can also improve the adhesion between the phases. On the other hand, the strength remained constant or even levelled off a bit when the amount of wood flour was increased from 39 to 44% in the crosslinked composites. A possible explanation for this could be related to not having achieved good enough dispersion during processing of the composites with 44% wood flour. The higher flexural strength in the sauna-stored samples compared to the ones stored at room temperature could be explained by the higher degree of crosslinking in the sauna-stored samples (see Table 2). Without interfacial adhesion, the strength would remain constant or decrease as is the case for the non-crosslinked composites. The improved adhesion between wood and polyethylene in the crosslinked composites is also believed to explain the superior flexural strain before break. All the crosslinked composites could be stretched more than 5% and most of the samples did not break at all during the experiment. The non-crosslinked, on the other hand, all broke during the experiment and usually at a strain level less than 3%. Without interfacial adhesion, the gap between the wood and polyethylene phases, provides an area of weakness which easily propagates a crack through the material. As can be seen in Fig. 8, the flexural modulus for the non-crosslinked samples increases with an increased amount of wood flour. In the crosslinked samples, the modulus increases as the amount of wood flour is increased up to 39% and then levels off or remains constant. Moreover, the flexural modulus of the silane crosslinked samples is lower than for the non-crosslinked ones. Earlier work on silane crosslinked polyethylene-wood flour composites did not show a decrease in modulus upon crosslinking [23]. Kuan et al. [23] treated wood flour with 2 phr (parts per hundred parts of resin) of VTMS before compounding with polyethylene in an extruder and thereafter injection moulding. In their study the water crosslinked

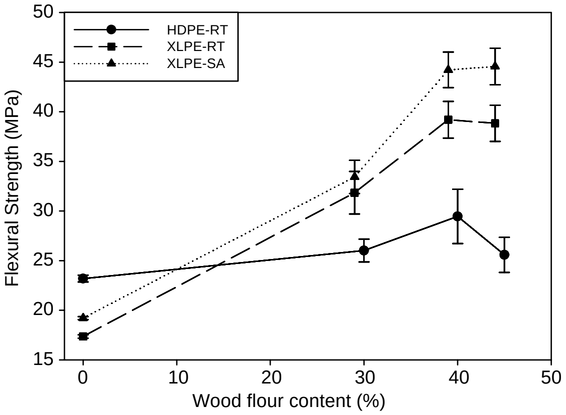

Fig. 7. Average values of flexural strength as a function of wood flour content.

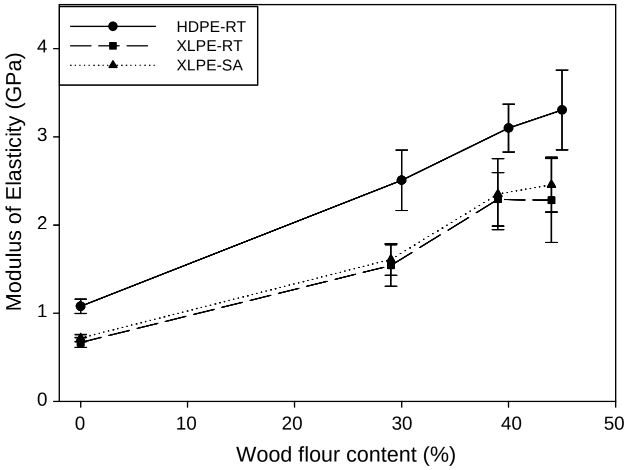

Fig. 8. Average values of flexural modulus as a function of wood flour content.

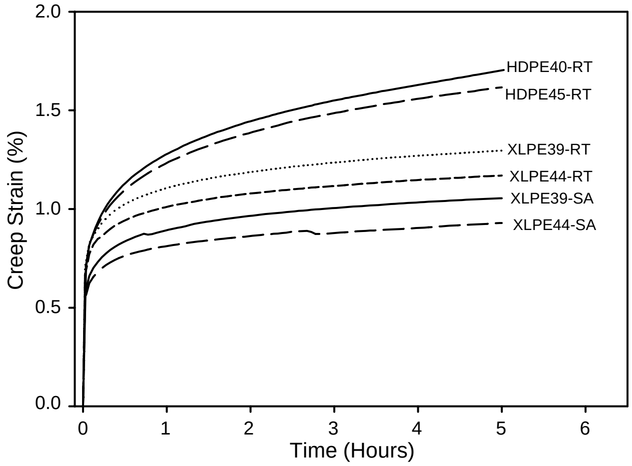

Fig. 9. Strain as a function of time during creep experiments at 30°C. The applied static stress was 5 MPa.

composites showed higher flexural modulus than the non-crosslinked. The modulus is strongly affected by the filler level and the orientation of the filler and less by the polymer–wood fibre adhesion [32]. The lower crystallinity of the polyethylene matrix and the plasticising effect of un-reacted silane in the crosslinked samples are believed to explain why they have a lower flexural modulus than do the non-crosslinked samples. All the mechanical data from the flexural test are summarised in Table 4.

3.5.2. Impact strength

The results from the impact strength test are presented in Table 4. As can be seen in the table the silane crosslinked composites with 29% wood flour have at least 300% higher impact strength than the non-crosslinked composites. With increased wood flour content in the composites, the impact strength decreases, but the crosslinked composites still have higher impact strength than do the non-crosslinked ones. The toughness of filled polymers can be improved in several ways: (1) increase the matrix toughness, (2) optimise the adhesion between filler and matrix (3) optimise the filler related properties such as filler content, particle size, and dispersion [14]. Crosslinking of the matrix is one way of improving the toughness of the polymer matrix. There is also indication of improved adhesion between the wood flour and the polyethylene matrix in the crosslinked composites. Thus, a possible explanation for the improved toughness of the silane crosslinked composites could be a toughening of the matrix and enhanced adhesion between wood and polyethylene upon crosslinking.

Table 4
Mechanical properties of neat plastics and composites

Sample code	Flexural properties Strength (MPa)	Modulus (GPa)	Strain (%)	Impact Strength Izod (J/m)
XLPE-RT	17.4±0.2	0.7±0.1	>5	–
XLPE29-RT	31.8±2.1	1.5±0.2	>5	209.5±33.5
XLPE39-RT	39.2±1.9	2.3±0.3	>5	141.0±20.7
XLPE44-RT	38.8±1.8	2.3±0.5	>5	131.3±16.6
XLPE-SA	19.2±0.2	0.7±0.0	>5	–
XLPE29-SA	33.4±1.7	1.6±0.2	>5	235.9±28.8
XLPE39-SA	44.2±1.8	2.4±0.4	>5	143.3±16.9
XLPE44-SA	44.6±1.8	2.5±0.3	>5	139.0±14.9
HDPE-RT	23.2±0.4	1.1±0.1	>5	–
HDPE30-RT	26.0±1.2	2.5±0.3	2.9±0.3	57.5±9.6
HDPE40-RT	29.5±2.7	3.1±0.3	1.8±0.1	54.1±17.0
HDPE45-RT	25.6±1.8	3.3±0.5	1.7±0.2	49.5±12.7

3.5.3. Short-term creep/creep cycling

In Fig. 9, the results from the short-term creep test are shown. For both the non-crosslinked and crosslinked composites, the creep response is slightly lower for those with 44–45% wood flour content than those with 39–40%. Thus, the addition of wood filler to the polymer matrix has a positive effect on lowering the creep, a phenomenon that has been reported in earlier studies [17,18]. The lower creep response in the crosslinked composites with 44% wood flour compared to the ones with 39%, could be due to higher amount of wood flour but also due to a slightly different gel content in the samples. Moreover, the creep response of the crosslinked composites is significantly lower than for the non-crosslinked composites. The creep response in the sauna-stored composites was also lower than for the samples stored at room temperature. The degree of crosslinking in the sauna-stored composites is higher than in the ones stored at room temperature and could thus explain the lower creep response. The lower creep in the crosslinked composites compared to the non-crosslinked composites can be related to a reduced viscous flow due to crosslinking as well as improved adhesion between the polyethylene matrix and wood flour.

A crosslinked sample that has been stored in a sauna (24 h) and a non-crosslinked sample that has been stored in room temperature (24 days) were also subjected to creep

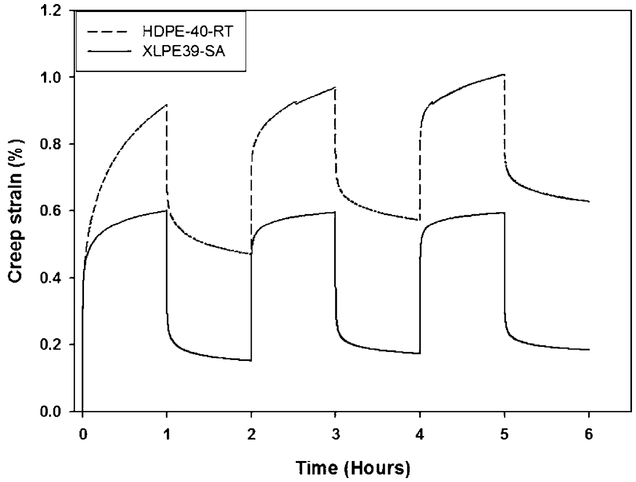

Fig. 10. Strain as a function of time during creep cycling experiments at 60°C. The applied static stress during loading was 2 MPa.

cycling. A 2 MPa stress was applied on the samples at 60°C for 1 h and then released for 1 h and then applied again. This procedure was repeated three times. The results from the test are presented in Fig. 10. Once again, the creep response is higher for the non-crosslinked sample than for the crosslinked sample. It is also interesting to study the relaxation process after the stress has been released. A truly elastic material would recover completely when the stress is removed [26]. However, a viscoelastic material will have an immediate elastic recovery, a delayed elastic recovery and an unrecoverable part (viscous) [26]. As can be seen in the figure, the crosslinked samples have a more significant elastic response and the unrecoverable part after 1 h (delayed elastic and viscous) is less significant than for the non-crosslinked samples. Moreover, the unrecoverable part of the crosslinked samples does not increase to any great extent over cycles two and three. The unrecoverable part of the non-crosslinked sample, on the other hand, increases more significantly from cycle one to cycles two and three. The silane crosslinked composites thus not only lower the total amount of creep during loading but also decrease the unrecoverable part during creep cycling.

3.6. Fourier transform infrared spectroscopy

FTIR analysis was used for studying the crosslinking reaction in the composites, i.e. the formation of wood–O–Si bonds and Si–O–Si bonds. Subtraction spectra of crosslinked composites and non-crosslinked composites with 39–40% wood flour are shown in Fig. 11 a–c. Fig. 11a shows the subtraction spectrum of a crosslinked sample (gel content = 51%) and a non-crosslinked sample, both stored at room temperature for 24 days. The peak at 1092 cm^{-1} was related to residual un-hydrolysed Si–O–CH$_3$ groups [22,33]. As can be seen in the figure the area of this peak is rather large, suggesting a quite large amount of non-crosslinked and/or un-reacted silane. The small peak at 1012 cm^{-1} was attributed to un-reacted Si–OH groups [33]. The shoulder to the left (~1030 cm^{-1}) of the 1092 cm^{-1} peak was attributed to stretching of Si–O–Si bonds [22,33,34]. The relatively large peak around 1192 cm^{-1} has been reported earlier [33,35,36] to be caused by stretching of Si–O–Si and/or Si–O–C bonds. Thus, the peak at 1192 cm^{-1} could not only be related to both polysiloxanes (Si–O–Si) but also to covalent bonding between wood and silane (Si–O–C) or originate from residual un-hydrolysed Si–O–CH$_3$ groups. Additionally, bands corresponding to Si–O–Si symmetric vibrations are located at 800 cm^{-1} [29]. In Fig. 11b the subtraction spectra of a crosslinked composite stored in a sauna for 24 h (gel content = 72%) and a non-crosslinked composite stored at room temperature (24 days) is shown. The peak at around 1192 cm^{-1} has almost disappeared, which indicates that this peak probably corresponds to un-hydrolysed Si–O–CH$_3$. The broad band between 950 and 1150 cm^{-1} was related to a combination of Si–O–CH$_3$ groups and Si–O–Si bonding. The peaks at 800, 1056, 1039, 1111 and 1050 cm^{-1} were attributed to polysiloxanes (Si–O–Si), while the peak at 1091 cm^{-1} was attributed to Si–O–CH$_3$ [22,29,33]. Although the gel content of the sauna-stored composite was as high as 72%, there were still peaks corresponding to un-hydrolysed Si–O–CH$_3$ groups. The Si–O–CH$_3$ groups could originate from grafted groups that still are un-hydrolysed or from un-reacted silane in the samples. Fig. 11c shows subtraction spectra of the two crosslinked samples, the one stored in sauna minus the one stored at room temperature. The peaks in the spectrum between 950 and 1150 cm^{-1} can all be attributed to Si–O–Si bonding. This correlates well with the gel content of the samples with higher degree of crosslinking in the composite stored in sauna than in the one stored at room temperature.

3.7. Electron probe microanalyser

X-ray mapping of silicon at polished cross-sections of the composites was performed with an EPMA. The mapping was performed with the aim of trying to find where the silane was located in the composites. Fig. 12a–c shows the results of the mapping of the silicon signal for both crosslinked (room temperature and sauna-stored) and non-crosslinked composites. Although only selected parts of the composites are shown in the figures, these are assumed to be as representative of the sample as possible. Fig. 12a shows mapping of a selected area of a non-crosslinked composite with 40% wood flour. The micrograph shows the selected area of mapping and where the silane was found in a red colour scale. As can be seen in Fig. 12a, the amount of silane in the non-crosslinked samples is negligible. This would be expected since no silane was added to these samples and wood in its native form only contains traceable (<0.1%) of SiO_2 that could give Si-signal. Fig. 12b shows a crosslinked sample with 39% wood flour that has been stored at room temperature for 24 days (gel content = 51%). As can be seen in the figure, the amount of silane is now much higher. It is

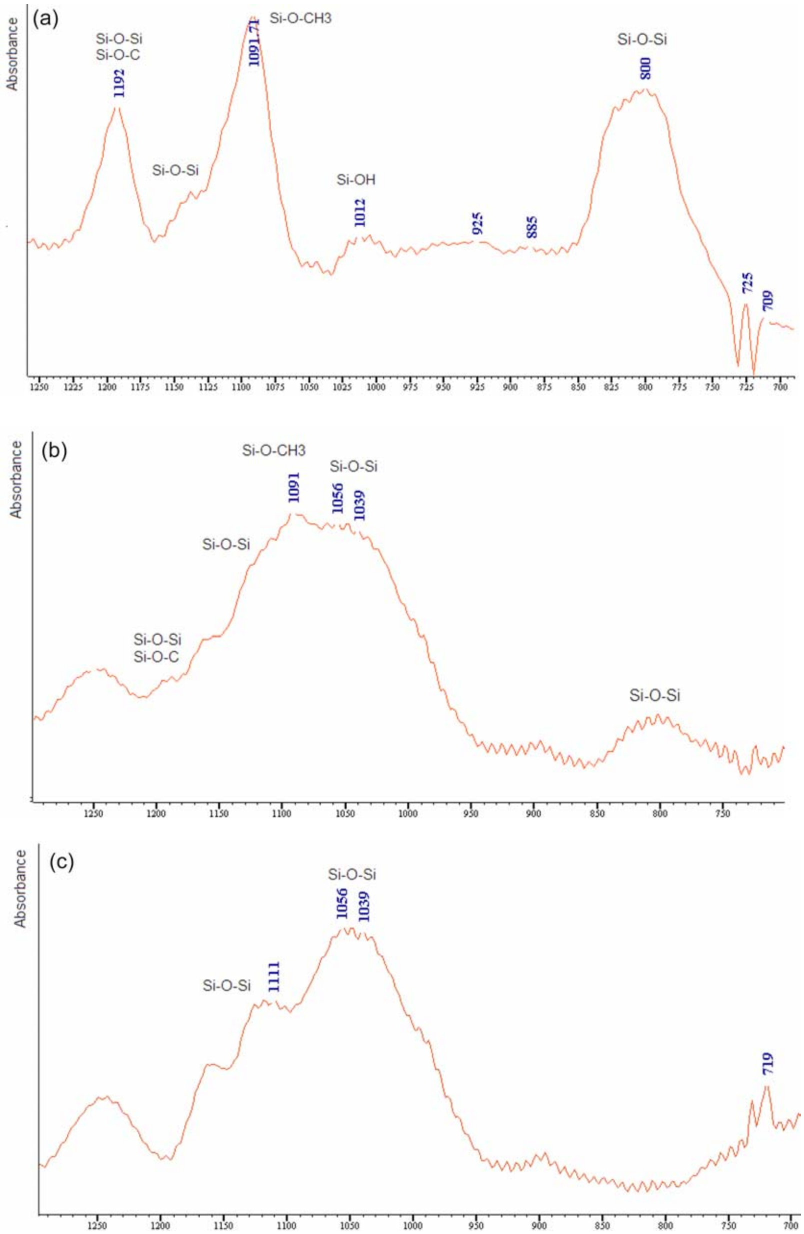

Fig. 11. FTIR subtraction spectra of (a) XLPE39-RT-HDPE40-RT (b) XLPE39-SA-HDPE40-RT (c) XLPE39-SA-XLPE39-RT.

also interesting to see that most of the silane is located in close vicinity of the wood fibre and in the fibre lumen. There are also a lot of small dots of silane evenly spread out in the matrix, but the main part of the silane is located in close proximity to the wood fibre. Fig. 12c also shows a crosslinked sample with 39% wood flour but stored in a sauna for 24 h (gel content = 72%). As can be seen in the figure, the amount of silane in this sample is also much higher than in the non-crosslinked one. The main part of the silane is also here in close proximity to the wood fibre and, also here, inside the fibre lumen. The silane can also be found at the interphase between the wood fibre and the polyethylene matrix. However, it is also here possible to see small dots of silane spread out in the matrix. The average amount of silane and its location were very similar for the crosslinked samples (both sauna and room temperature stored) as shown by a wider range of micrographs. There are many possibilities for the silane found around and inside the wood fibres to interact with the wood surface. It can be chemically bonded to the wood surface through either free radical or condensation reaction. Moreover, it can interact through hydrogen bonding between silanol groups (Si–OH) and the hydroxyl groups on wood. Without knowing the exact contribution from each bonding mechanism, the improved toughness of the crosslinked composites is most likely caused by improved interfacial adhesion between

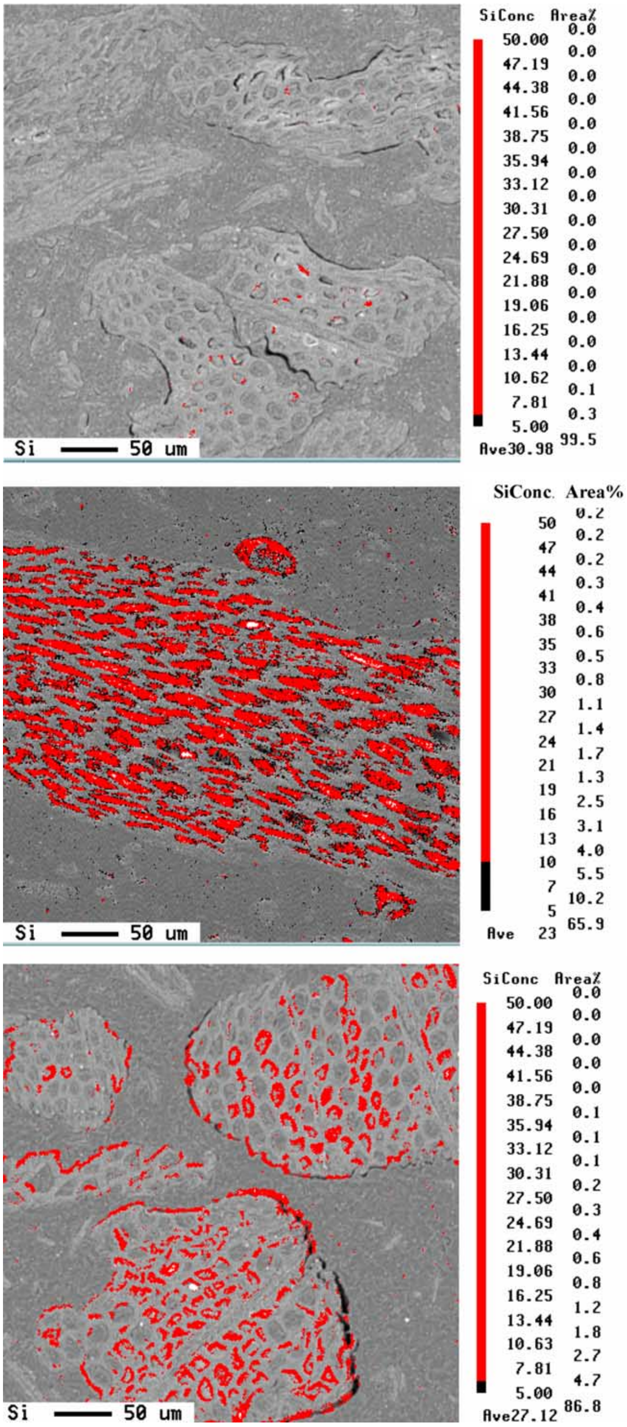

Fig. 12. X-ray mapping of silicon at polished cross-sections of the composites with an electron probe microanalyser, (a) HDPE40-RT (b) XLPE39-RT (c) XLPE39-SA.

the wood and polyethylene phases. Even though the main part of the silane was found in close vicinity of the wood fibres, there were also small dots of silane evenly spread out in the matrix (might be hard to see in the micrographs). The rather high gel contents in the samples (51 and 72%) show that the amount of silane in the samples is enough to fully crosslink them. The crosslinked composites have chemical bonding between the polymer chains but there might also be chemical bonding to wood thereby including wood in the network. FTIR data indicate that some of the silane remains un-reacted. That the lower flexural modulus in the crosslinked samples is lower than the modulus in the non-crosslinked ones could be related not only to lower crystallinity, but also to plastification by un-reacted silane. It is thus proposed that part of the silane is grafted onto polyethylene and wood thereby creating a crosslinked network in the matrix with chemical bonds (covalent and hydrogen bonding) to wood. The other part of the silane remains un-reacted and blends into the system.

4. Conclusions

Silane crosslinked composites were successfully produced in a one-step process. The crosslinking was shown to be initiated already during the compounding process in the extruder. Storage of the silane modified composites in a sauna at 90°C resulted in a gel content above 70% in all the composites already after 24 h. A maximum gel content (~80%) in the sauna-stored samples was reached between 24 and 72 h. Storage at room temperature did not seem to significantly influence the gel content of the composites. The flexural strength and elongation at break was significantly higher in the silane crosslinked composites than in the non-crosslinked ones. The flexural strength in the crosslinked composites increased with increased wood flour loading from zero to 39% and then levelled off. The improved toughness in the crosslinked composites is most likely caused by improved adhesion between the wood and polyethylene phases. The flexural modulus, on the other hand, was lower in the crosslinked samples than in the non-crosslinked ones. A lower crystallinity in the crosslinked samples is believed to be one explanation to the lower modulus. Plastification of un-reacted silane might also be an explanation for the lower modulus. The crosslinked composites also showed significantly higher impact strength than the non-crosslinked ones. The improvement in impact strength could not only be due to enhanced adhesion between the phases, but could also be related to a strengthening of the matrix upon crosslinking. Moreover, short-term creep analysis showed that not only was the total amount of creep during loading lower in the crosslinked composites than in the non-crosslinked counterparts, but the unrecoverable part also decreased during creep cycling. The lower creep in the crosslinked composites can be related to a reduced viscous flow due to crosslinking, as well as to improved adhesion between the polyethylene matrix and wood flour. FTIR analysis of the crosslinked samples showed peaks corresponding to both un-hydrolysed Si–O–CH_3 groups and polysiloxanes (Si–O–Si). In the crosslinked sample stored in sauna with a higher gel content, peaks corresponding to polysiloxanes (Si–O–Si) were more prevalent. X-ray microanalysis of the composites showed that most of the silane was found in close proximity to the wood fibre, both around and inside the wood fibres. It was also possible to locate silane evenly spread out in the matrix. This study provides a basis for proposing, that part of the silane is grafted onto polyethylene and wood thereby creating a crosslinked network in the matrix with chemical bonds (covalent and hydrogen bonding) to wood. The other part of the silane remains un-reacted and blends into the system.

This study is to be followed by a more throughout investigation where the amount of silane and processing conditions are optimised. In such a study, it would also be interesting to investigate other effects such as crosslinking density and possible variation in the degree of crosslinking over the thickness of the samples.

Acknowledgements

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Paper III

Silane crosslinked wood plastic composites; Processing and properties

Silane Crosslinked Wood Plastic Composites; Processing and Properties

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Keywords: A. Polymer-matrix composites (PMCs); B. Creep; B. Durability; E. Extrusion; Crosslinking

Introduction

Wood plastic composites have made significant gains in popularity over the last decade. Advantages of using wood as reinforcing filler in plastics include low cost, high relative strength and stiffness, low density and the fact that it is a natural resource [1-5]. Wood plastic composites are used to replace impregnated wood in many outdoor applications, because of recent regulations of the wood preservative industry. Wood plastic composites can also replace neat plastics in applications where the increase in stiffness accompanying the addition of wood fibre is an advantage. When proper coupling agents are used to improve fibre-matrix adhesion, wood can also be used as reinforcement to the plastic. The elasticity of wood fibre is approximately forty times greater than that of polyethylene and the overall strength is about twenty times higher [6]. There are also environmental reasons for replacing part of the plastic with wood.

Challenges for wood plastic composites include improving the toughness, reducing the weight and improving the long-term properties. There has been a lot of research over the past decades on different types of coupling agents to improve the adhesion between the wood and the plastic. One the most commonly used coupling agent is maleated polyethylene or polypropylene [2, 7-11]. There have also been some studies on other coupling agents such as isocyanates [12-13] and silanes [12-14]. In general, the use of these coupling agents significantly improves the toughness of wood plastic composites. In our previous studies we have also seen that silane crosslinking significantly improved the toughness of wood plastic composites [15-16]. Reducing the weight of wood plastic composites is another challenge for these materials. The density of wood plastic composites is almost twice that of solid lumber [17]. The concept of creating cellular foamed structures has been shown to greatly reduce the weight of wood plastic composites [17-18]. Hollow or shaped cross sections can also be used to reduce the weight of the composites [19]. Furthermore, improvements in long-term properties such as durability during outdoor exposure and long-term load performance are necessary. Exposure to ultraviolet (UV) radiation and moisture during outdoor use is of particular concern for wood plastic composites [20]. Thermoplastics typically perform poorly in long-term loading because linear polymer molecules exhibit a strong time and temperature dependent response. Addition of wood filler to the polymer matrix decreases creep response during loading [15-16, 21], but it is still a problem. Crosslinking of the polymer matrix has shown to be one way of reducing creep during long-term loading [15-16].

The use of silane technology in crosslinking polyethylene was introduced in the seventies to improve the temperature durability of polyethylene. Vinyltrimethoxy silane can be melt-grafted onto polyethylene in presence of small amounts of peroxide. At elevated temperature the peroxide first decomposes and creates radicals. These radicals have the potential to abstract hydrogen from the polyethylene polymer but can also attack the vinyl group of the vinyltrimethoxy silane molecule and convert it into radicals. These free radicals either combine with one another or attack another molecule in the same fashion to propagate the free-radical reaction [22]. This process results in grafting of vinyltrimethoxy silane onto polyethylene; this is a prerequisite for crosslinking the material. Fig. 1a shows the reaction mechanism during peroxide-induced melt grafting of vinyltrimethoxy silane onto polyethylene. The most prominent side reaction during melt grafting of vinyltrimethoxy silane onto high density polyethylene is crosslinking or branching caused by radical-radical combination [23]. Fig. 1b) shows the reaction mechanism caused by radical induced crosslinking of polyethylene. Some of the crosslinked network in the specimens is thus caused by a radical-radical combination. The silane crosslinking reaction takes place in the presence of trace amounts of water and the reactions can be accelerated by incorporating a tin based catalyst. The silane crosslinking reaction proceeds over two steps as is shown in Fig. 2. In the first step the methoxyl groups are hydrolysed to hydroxyl groups during leaving of methanol. The crosslinking takes place in the second step where the hydroxyl groups recombine through a condensation step [24].

Addition of wood flour during the melt grafting step makes it possible to graft vinyltrimethoxy silane onto both polyethylene and the wood flour. Moreover, there is a possibility of a direct condensation reaction between silanol groups (Si-OH) and hydroxyl groups on wood. This creates a covalent bonding between wood and the silanol group (wood-O-Si), where the vinyl group can be chemically bonded (covalent C-C) or interact through van-der-Waals forces with the polyethylene matrix. In a previous study, we showed that the toughness of silane crosslinked composites was significantly higher than for the non-crosslinked [16]. This was explained as a result of improved adhesion between the polyethylene and wood flour phases. Kuan et al. [25] studied silane crosslinked polyethylene-wood flour composites. The wood flour was treated with vinyltrimethoxy silane before compounding with polyethylene. The crosslinking was subsequently initiated by water treatment. Water crosslinked samples exhibited better mechanical properties than the non-crosslinked samples as a result of chemical bonding between both wood and polyethylene. There are also other studies were peroxides have been used to crosslink composites of polyethylene and wood flour / pulp [26-27]. The mechanical properties of the crosslinked composites were improved compared to the non-crosslinked. Crosslinking was shown to improve adhesion between polyethylene and wood filler as a result of recombination of radicals formed at the filler surface and polyethylene macro radicals.

This study is focusing on process optimization and evaluation of mechanical properties of silane crosslinked composites. The process optimization includes choosing a suitable processing method and finding the optimum level of silane addition. The silane grafted composites are stored at different humidity to study how that affects the degree of crosslinking in the composites. Silane crosslinked composites with different degree of crosslinking are then evaluated regarding their mechanical performance. This study is a continuation of an earlier article [16].

2. Experimental

2.1. Materials

High density polyethylene, HDPE MG9601 (MFI=31 g/10min, 190˚C/5kg), was purchased from Borealis AB (Stenungsund, Sweden). Wood flour from softwood (spruce and pine) was kindly provided by Scandinavian Wood Fiber AB (Orsa, Sweden). According to the supplier, the size of the softwood wood flour was 200-400 µm. The shape of the wood flour was fractured fibre bundles. Vinyltrimethoxy silane 98 % was purchased from Sigma Aldrich (Leirdal, Norway). Dicumyl peroxide, Perkadox BC-FF 99%, was kindly supplied by Akzo Nobel (Gothenburg, Sweden). Throughout this paper the crosslinked samples are at some places referred to as "XLPE" and the non-crosslinked as "HDPE". Samples stored at room temperature and in a sauna are abbreviated RT and SA, respectively.

2.2. Processing

The wood flour was dried for 24 hours at 100 ˚C to a moisture content of ~0.3 % (based on dry weight) before processing. Plastic granulates and wood flour were compounded using a Coperion Werner and Pfleiderer ZSK 25 WLE (Stuttgart, Germany) corotating twin-screw extruder. The plastic and the wood flour were fed to the extruder by the use of K-tron gravimetric feeders (Niederlenz, Schwitzerland). Feeding of the wood flour was performed at temperature zone 4 through a twin-screw side feeder operating at 100 rpm. Fig. 3, shows the processing parameters during compounding. The temperatures were between 165-200 ˚C, the screw speed was 100 rpm, the melt pressure at the die varied between 6-65 bar depending on material blend, and the material output was 6 kg/h. Silane crosslinked materials 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 in the samples was 0, 2, 3, 4 and 6 % w/w. Vacuum venting at temperature zone 10 was used to minimize volatile extractives and un-reacted silane in the final samples. The samples were extruded through a rectangular die with the dimensions of 5 × 30 mm and cooled in ambiently. The extruded materials were subsequently compression moulded (Schwabenthan, Table Press Polystat 200T, Germany) to a thickness of approximately 3 mm to be able to make samples for mechanical testing. Compression moulding was performed at 190 ˚C with no pressure for 5 min, then 2.5 min with 100 bar pressure and finally 2.5 min with 200 bar pressure. Standard test specimens for mechanical testing were cut from the compression moulded samples. The processing formulations are shown in Table 1. Part of the compression moulded samples was stored at room temperature and the others were stored for 48 hours in a simulated sauna. The storage conditions in the sauna were approximately 100 % RH and 90 ˚C. The sauna stored samples were subsequently dried to their initial weight before testing.

2.3 Gel content

The gel content of the samples was determined using p-xylene extraction according to ASTM standard 2765. 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 crosslinking 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 hours. Extracted specimens were then dried at 150 ˚C until a constant weight was attained and subsequently re-weighed. The gel content of the different blends was determined as the average of two separate analyses. The gel-content was calculated according to the following equation:

Extract % = (weight lost during extraction) / (weight of original specimen-weight of filler)

Gel content = 100 – Extract % (1)

2.4 Swell ratio

The swell ratio of crosslinked composites in hot p-xylene for 24 hours was determined in accordance with ASTM standard 2765. Specimens of the crosslinked composites were weighed, immersed in p-xylene at 110 °C for 24 hours, removed, weighed in the swollen state, dried and reweighed. The swell ratio of the different blends was determined as the average of two separate analyses. The swell ratio was calculated as follows:

$$Swell\ \ ratio\% = \left(\frac{W_g - W_d}{W_o - W_e} \right) K + 1 \qquad (2)$$

W_g = weight of swollen gel after the immersion period

W_d = weight of dried gel

$W_o = f \times W_s$

f = polymer factor (the ratio of the weight of the polymer in the formulation to the total weight of the formulation).

W_s = weight of specimen being tested

W_e = weight of extract (amount of polymer extracted from the specimen in the test)

K = ratio of the density of the polymer to that of the solvent at the immersion temperature. This ratio is 1.17 for HDPE at 110 °C.

2.5 Mechanical testing

2.5.1 Flexural properties

Flexural properties of the samples were measured on a Tinius Olsen H5K-S UTM equipment (Horsham, PA, USA) in accordance with ASTM D790. The dimensions of the specimens tested were approximately 3.2×12.7×130 mm. The measurements were performed at ambient conditions, i.e. a temperature of 22 ˚C and a relative humidity of approximately 40 %. At least five specimens of each blend were tested.

2.5.2 Impact Strength

Izod impact strength of un-notched composite specimens was tested on an Otto Wolpert-Werke **(**Ludwigshafen, Germany) instrument in accordance with ASTM D256-97. The dimensions of the specimens tested were approximately 3.2×12.7×50 mm. The measurements were performed at ambient conditions, i.e. a temperature of 22 ˚C and a relative humidity of approximately 40 %. The impact energy was divided by the width of the specimens to yield impact strength (J/m). At least eight specimens of each blend were tested.

2.5.3 Creep properties

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 1.6×12×30 mm. The applied static stress was fixed at 5 MPa and the temperature was fixed at 30 ˚C.

2.6 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) tests were performed on a DSC-7 (Perkin Elmer, Germany) with samples of approximately 10 mg sealed in aluminium pans. The samples were analysed under nitrogen atmosphere in a temperature range between 25-160 °C at a heating range of 10 °C/min. The melting temperature and melting enthalpy of the samples were determined. The crystallinity of the samples was calculated according to the following equation:

$$Crystallinity\ (\%) = \frac{\Delta H_{melting,\ sample}\ (J/g)}{\Delta H_{melting,\ 100\%\ crystalline\ polyethylene}\ (J/g)} \qquad (3)$$

A melting enthalpy of 290 J/g for 100 % crystalline polyethylene was used in the calculation of crystallinity [28]. A compensation for the wood flour content was made while calculating the melting enthalpy of the composites. The melting temperature and melting enthalpy of the different blends were determined as the average of three separate analyses.

3. Results and Discussion

3.1. Grafting process

Preparation of silane grafted composites can be performed in different ways. The plastic (or wood flour) can be treated with a diluted solution of vinyl silane/peroxide and the solvent subsequently evaporated before processing. Drawbacks of this method include the use of solvent and that the process is time consuming. Kuan et al. treated wood flour directly with vinyltrimethoxy silane without the use of solvent [25]. Another method is to pump the vinyl silane/peroxide solution directly into the extruder during processing. This can be done in a two step process where the first step includes silane grafting of neat plastic and the second step incorporation of wood flour. This procedure was used in our first study of silane crosslinked composites [15]. In this study, the silane grafting and composite production were carried out simultaneously in a one step process. By doing so, the production of composites is more economical, industrially friendly and also gives the possibility of grafting silane onto both polyethylene and wood flour.

Processing of crosslinked composites was found to be more difficult than processing of the non-crosslinked. Addition of vinyltrimethoxy silane and dicumyl peroxide solution during processing significantly increased the motor load and melt pressure in the extruder. An increase in melt viscosity of polyethylene upon silane grafting was expected. This increase in melt viscosity is due to premature crosslinking but melt viscosity will also increase as a result of interaction between grafted silane groups [23]. The increase in melt viscosity and the volatile compounds created during melt grafting reactions contribute to the increased melt pressure. Higher melt pressure occurred with an increased addition of silane solution and reached a maximum at 65 bar when 6 % w/w of silane solution was added. Fig. 4, shows the extruded profiles at different levels of silane solution addition. As can be seen in the figure, addition of 2 % w/w silane solution produced some minor edge tearing of the extruded profiles. At an increased level of added silane solution the edge-tearing became more significant. At 4 and 6 % w/w of added silane solution the surfaces of the profiles also became rough. Difficulties in encapsulating the wood at the surfaces of the profile are believed to be the reason for edge tearing and rougher surfaces of the crosslinked composites. The increase in melt viscosity upon silane grafting can explain the encapsulating difficulties. Addition of lubricant during processing might eliminate these problems. To avoid the risk of interference between the silane/peroxide solution and the lubricant, no lubricant was used in this study.

3.2. Degree of crosslinking

The degree of crosslinking in the composites was determined by gel content and swell ratio measurements. The gel content and swell ratio was determined in accordance with ASTM standard 2765. Crosslinked polyethylene is insoluble in boiling p-xylene while the non-crosslinked part is soluble. The gel content can thus be determined gravimetrically from the extracted samples. The swell ratio of the crosslinked composites in hot p-xylene was determined in order to study the correlation between gel content and network density. Storage at environments with different humidity levels i.e. in a simulated sauna and at room temperature, affected the degree of crosslinking in the samples. As can be seen in Fig. 2, the first step in the crosslinking reaction is hydrolysis of the methoxyl groups to silanol groups. Water is responsible for the hydrolysis of the methoxyl groups. A higher humidity level would thus be expected to create a higher degree of crosslinking in the samples. As can be seen in Table 2, storage in a high humidity sauna generated a higher degree of crosslinking in the composites than storage at room temperature. The swell ratio is also significantly lower in the sauna stored composites. This is evidence of a higher network density in the sauna stored composites. In a previous study it was shown that storage of silane modified composites at room temperature did not significantly affect the gel content in the composites [16]. The degree of crosslinking in the composites stored at room temperature is thus believed to correspond to the crosslinking that takes place during processing. A higher gel content with an increased addition of silane solution was found in the composites stored at room temperature. The swell ratio follows the same trend, with a decrease in swell ratio upon increased addition of silane solution. This shows that a higher level of silane addition during processing increases the crosslinking that takes place during processing. Moreover, storage of the composites in a sauna significantly increased the gel content and decreased the swell ratio of the composites. In the composite to which 2 % w/w of silane solution was added during processing, the gel content after storage in a sauna was lower (61 %) than composites with a higher level of silane addition. The sauna stored composites with 3, 4 and 6 % w/w of added silane during processing all had a gel content in the range between 69 to 74 %. Earlier studies have shown that the maximum gel content during silane crosslinking is in the range between 75-80 % [16, 24]. An addition of 4 % w/w or more of the silane solution during processing thus seem necessary to fully crosslink the composites in a sauna within 48 hours. In our previous study, the degree of crosslinking as a function of storage time in a sauna was investigated for composites to which 9 %w/w of silane solution was added [16]. Composites with 44 % wood flour reach the maximum gel content already after 24 hours in the sauna while the composites with 29 and 39 % wood flour reach the maximum gel content between 24-72 hours. In Fig. 5, the swell ratio as a function of gel content is shown. As can be seen in the figure, there is a linear relationship between swell ratio and gel content. A higher gel content is thus evidence of an increased network density. The network density is thus highest in the sauna stored composites to which 4 % w/w or more of silane solution was added during processing.

3.3 Mechanical properties

3.3.1. Flexural properties

All the mechanical data from the flexural testing are summarised in Table 3. In Fig. 6, typical stress-strain curves for composites and neat plastics are shown. As can be seen in the figure, the flexural strength and modulus of neat HDPE is higher than in neat XLPE. In contrast to the neat plastics, the crosslinked composites showed flexural strength superior to the composites to which no silane was added. The improved strength in the crosslinked composites is most likely caused by improved adhesion between wood and polyethylene. Consequently, even though the flexural strength of the neat crosslinked polyethylene matrix was lower than for the non-crosslinked, the flexural strength was significantly higher in the crosslinked composites than in the non-crosslinked composites. Improved adhesion between wood and plastic makes it possible for stress transfer from the weaker plastic matrix to the stronger wood fibre during loading, thereby improving the strength of the crosslinked composites. The improved adhesion could be due to covalent bonding between wood and 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. Without interfacial adhesion, the strength would decrease upon addition of wood flour as is the case for the non-crosslinked composites. Average values of the flexural strength as a function of silane solution addition are shown in Fig. 7. The flexural strength in the crosslinked composites reached a maximum between 2-3 % w/w of added silane and then decreased with further addition of silane solution. The flexural strength in crosslinked composites stored at room temperature did not differ much from the ones stored in a sauna. This indicates that the reactions responsible for improving the adhesion between wood and polyethylene mainly takes place during the higher temperature used under processing. The improved adhesion between wood and polyethylene in the crosslinked composites is also believed to explain the superior flexural strain before break. All the crosslinked composites could be stretched more than 5 % and most of the samples did not break at all during the experiment. The non-crosslinked, on the other hand, all broke during the experiment and usually at a strain level less than 3 %. Without interfacial adhesion, the gap between the wood and polyethylene phases provides an area of weakness, which easily propagates a crack through the material. As can be seen in Fig. 8, the flexural modulus of the silane crosslinked composites is lower than for the non-crosslinked ones. Independent of storage conditions (i.e. at room temperature or in a sauna), the modulus also decrease with an increased amount of added silane.

3.3.2. Impact Strength

Izod impact strength of un-notched composite specimens was tested in accordance with ASTM D256. Impact testing was performed in order to study if the silane crosslinked composites could absorb more energy than the non-crosslinked during a fast strike. The results from the impact testing are presented in Fig. 9 and Table 3. The impact strength was significantly higher (about three times) in the crosslinked composites than in the non-crosslinked. Improved adhesion between wood and polyethylene and improved impact strength of the polyethylene matrix upon crosslinking, can explain the superior impact strength of the crosslinked composites. It is hard to distinguish any trends in impact strength among the crosslinked composites when taking the standard deviation into account. However, the composites with 2 % of added silane solution stored in room temperature, seems to have slightly lower impact strength than the other. The degree of crosslinking in this composite was also shown earlier to be the lowest. This implies that the superior impact strength of the crosslinked composites is a result of both improved adhesion and the degree of crosslinking in the composites.

3.3.3. Short-term creep

Short-term creep experiments were performed using a dynamic mechanical thermal analyzer, DMTA V. The experiments were performed to study the effect of silane crosslinking on the creep properties of the composites. For the most general case of a linear viscoelastic material the total strain e is the sum of three essentially separate parts: e_1 the immediate elastic deformation, e_2 the delayed elastic deformation and e_3 the Newtonian flow, which is identical to the deformation of a viscous liquid obeying Newton's law of viscosity [29]. The magnitudes of e_1, e_2 and e_3 are exactly proportional to the magnitude of the applied stress, so that a creep compliance $J(t)$ can be defined, which is the function of time only:

$$J(t) = \frac{e(t)}{\sigma} = J_1 + J_2 + J_3 \qquad (4)$$

where J_1, J_2 and J_3 corresponds to e_1, e_2 and e_3 [29]. Crosslinked polymers do not show a J_3 term, and to a very good approximation neither do highly crystalline polymers. The creep modulus, Ec, represents the modulus of a material at a given stress level and temperature over a specified period of time. Creep modulus is expressed as the inverse of the creep compliance [29].

In Fig. 10, the results from the short-term creep test of non-crosslinked and crosslinked (stored in a sauna) composites are shown. The final creep response in the crosslinked composites is significantly lower than in the non-crosslinked composite. A lower creep in the crosslinked composites compared to the non-crosslinked composites can be related to a reduced viscous flow of the matrix due to crosslinking as well as improved adhesion between the polyethylene matrix and wood flour. As can be seen in the figure, the final creep response in the crosslinked composites decreased with increased amount of added silane. However, the composite with 6 % w/w of added silane showed a slightly higher creep response than in the composite with 4 % w/w of added silane. There is a good correlation between the creep response and the degree of crosslinking in the composites. A higher degree of crosslinking (i.e. higher gel content) lowers the creep response in the composites. One would expect the creep response in the composites with 4 and 6 % w/w of added silane to show more similar creep behaviour since the gel content in these composites was equivalent. In an earlier study of silane crosslinked composites, it was also shown that a higher degree of crosslinking lowered the creep response [16]. In that study, crosslinked composites stored in a sauna showed lower creep response than composites stored at room temperature. In Fig. 10, the creep modulus of the composites seems to be in contradiction to the flexural modulus of the composites. It seems like the creep modulus is increasing with increased amount of added silane solution to the composites. However, studying the creep curves at a much shorter time period gave another picture. The instantaneous creep strain showed to be lowest for the non-crosslinked composites and then increased at higher level of silane addition. After a couple of seconds (< 5) the curves cross each other and the composites with low degree of crosslinking (low addition of silane solution) showed a higher creep strain than the ones with higher degree of crosslinking. The points collected during the first seconds of the experiment scatter and deviate from a straight line. This is probably caused by instrumental difficulties of reaching stable state. Due to this scattering, the creep modulus of the composites was not calculated.

3.4 Crystallinity

Differential scanning calorimetry (DSC) analyses were used to determine the crystallinity in the samples. The DSC measurements were performed to study if crosslinking affected the degree of crystallinity in the samples and thereby the mechanical properties. Fig. 11 shows the heating DSC thermographs of non-crosslinked and crosslinked composites stored at room temperature. As can be seen in the figure, the melting endotherm (ΔH_m) is lower in the crosslinked samples than in the non-crosslinked. This is evidence of a lower degree of crystallinity in the crosslinked samples. The crystallinity also decreases with increased amount of added silane to the samples during processing. The melting peak temperature of the crosslinked composites is also slightly lower than in the non-crosslinked one. In Table 4, the crystallinity, melting enthalpy and melting peak temperatures from the DSC analyses are summarised. Crosslinked composites stored in a sauna also showed lower crystallinity than the non-crosslinked composite stored at room temperature. Moreover, the crosslinked composites stored in a sauna showed a slightly higher crystallinity than the crosslinked composites stored at room temperature. The slightly higher crystallinity in crosslinked composites stored in a sauna can be related to some re-crystallization taking place during storage in a sauna at 90 ˚C. DSC analysis of the neat plastics also showed the same trend, with a lower crystallinity (56 %) in XLPE-4-RT compared to 65 % in HDPE-RT. Since silane crosslinking mainly takes place in the solid state, the crystalline phase should not undergo considerable changes, rather the crosslinking takes place only in the amorphous phase. However, as was shown in Table 2 (gel content) the crosslinking reaction is initiated already during extrusion. This initial crosslinking can be due to silane crosslinking but might also be due to side reactions as was described in the introduction section. The crosslinked polyethylene forms a network structure. The network structure makes the macromolecules chain less flexible, so the crystallization melt peak becomes lower and crystallization more difficult. A higher level of silane addition during processing increased the degree of crosslinking in the composites. This explains the decrease in crystallinity with increased amount of added silane to the composites. A lower crystallinity in silane crosslinked specimens has also been reported by other authors [28, 30].

The crystallinity results can help to explain the results from the mechanical testing. The lower strength and modulus of neat XLPE than of neat HDPE can thus be explained as a result of the lower crystallinity in the crosslinked polyethylene. Furthermore, the decrease in strength of the crosslinked composites after passing through the maximum between 2-3 %, can be explained to be caused by a decrease in crystallinity at higher level of silane addition. In Fig. 12, the flexural modulus as a function of the crystallinity in the composites is plotted. There is a linear relationship between the flexural modulus and the crystallinity in the composites. The decrease in crystallinity with increased amount of added silane to the composites is thus believed to explain the lowering in modulus.

4. Conclusions

Silane crosslinked composites with different amount of silane were produced in twin-screw extruder. Processing of the crosslinked composites was found to be more difficult than processing of the non-crosslinked. At a higher level of silane addition, edge-tearing became a problem and the extruded profiles got a rougher surface. The crosslinking was shown to be initiated already during the compounding process. Storage in a high humidity sauna at 90 ˚C generated a higher degree of crosslinking in the composites than storage at room temperature. An addition of at least 4 % w/w silane solution during processing was necessary to fully crosslink the composites in a sauna within 48 hours. Swelling experiment in hot p-xylene showed an almost linear relationship between swell ratio and gel content. The network density was highest in the sauna stored composites to which 4 % w/w or more of silane solution was added during processing.

The flexural strength and elongation at break was significantly higher in the silane crosslinked composites than in the non-crosslinked one. The improved toughness in the crosslinked composites is most likely caused by improved adhesion between the wood and polyethylene phases. The flexural strength in the crosslinked composites reached a maximum between 2-3 % w/w of added silane and then decreased with further addition of silane. The flexural modulus was lower in the crosslinked composites than in the non-crosslinked ones. Impact testing showed that the impact strength of the crosslinked composites was considerable higher (about three times) than the non-crosslinked. This was explained as a result of both improved adhesion and the degree of crosslinking in the composites. Moreover, short-term creep analysis showed that the creep response in crosslinked composites was significantly lower than in the non-crosslinked composite. The lower creep in the crosslinked composites was related to a reduced viscous flow due to crosslinking, as well as to improved adhesion between the polyethylene matrix and wood flour. There was a good correlation between the creep response and the degree of crosslinking in the composites. A higher degree of crosslinking in the composites lowered the creep response.

Differential scanning calorimetry measurements of the composites showed that the crystallinity of the polyethylene matrix was lower in the crosslinked composites than in the non-crosslinked. An increased amount of added silane was also found to decrease the crystallinity in the composites. The decrease in crystallinity was explained as a result of the initial crosslinking that took place during the processing, which made the macromolecules less flexible and crystallization more difficult. A linear relationship between the flexural modulus and the crystallinity in the composites was found. The decrease in crystallinity with increased amount of added silane was thus believed to explain the lowering in modulus.

This study provides a basis for proposing, that an addition of 4 % w/w or more of silane solution during processing is necessary to fully crosslink the composites in a sauna (90 °C, 100 % RH) within 48 hours. Considering the flexural strength and stiffness of the composites, an optimum addition of silane solution is in the range of 2-3 % w/w. On the other hand, if a low creep response in the composites is of first priority an addition 4 % w/w of silane solution is preferable.

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Figure 1. Bengtsson and Oksman

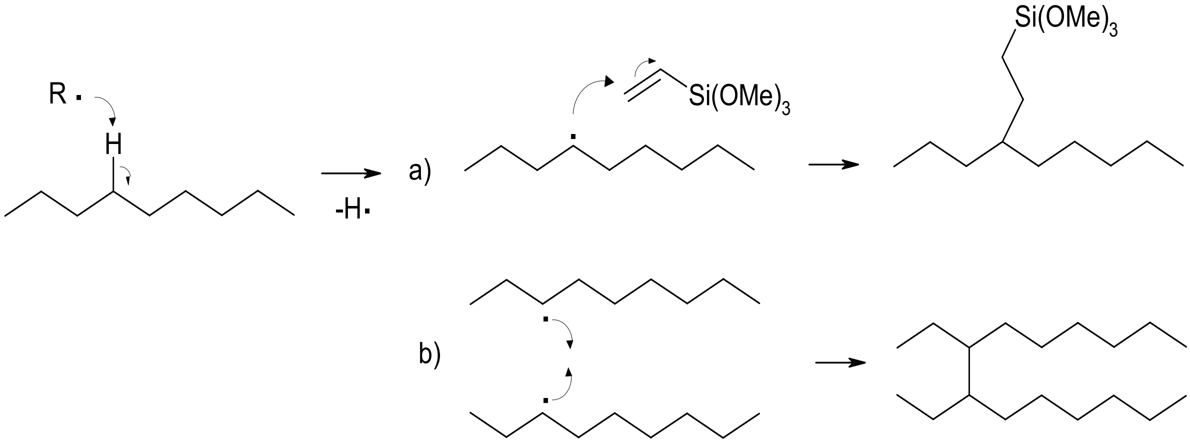

Fig. 1. The reaction mechanism during a) peroxide induced melt grafting of vinyltrimethoxy silane onto polyethylene, b) radical induced crosslinking of polyethylene

Figure 2. Bengtsson and Oksman

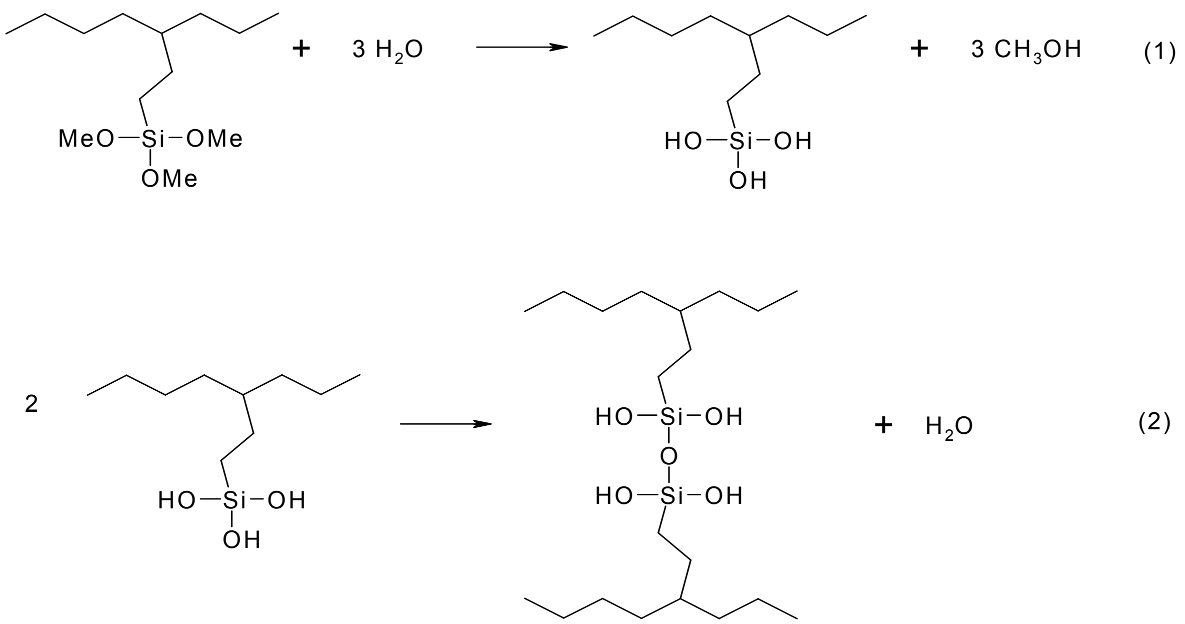

Fig. 2. The hydrolysis step (1) and condensation step (2) during silane crosslinking.

Figure 3. Bengtsson and Oksman

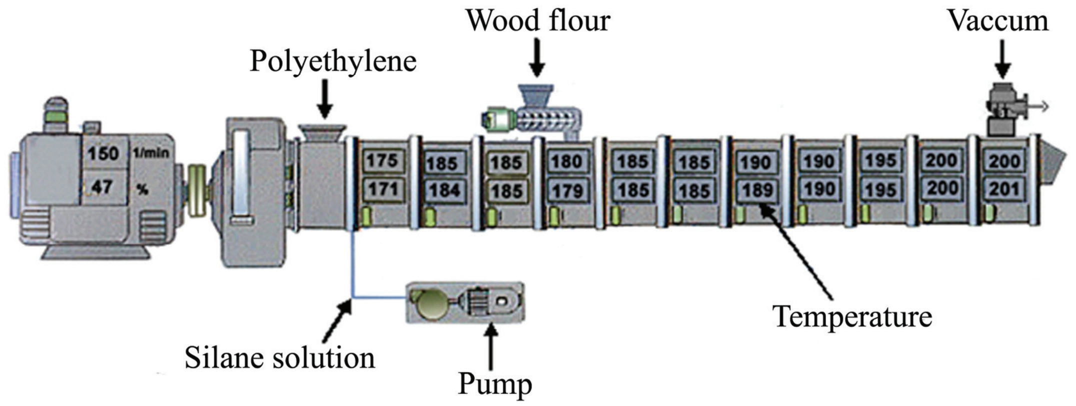

Fig. 3. Extruder setup during processing.

Figure 4. Bengtsson and Oksman

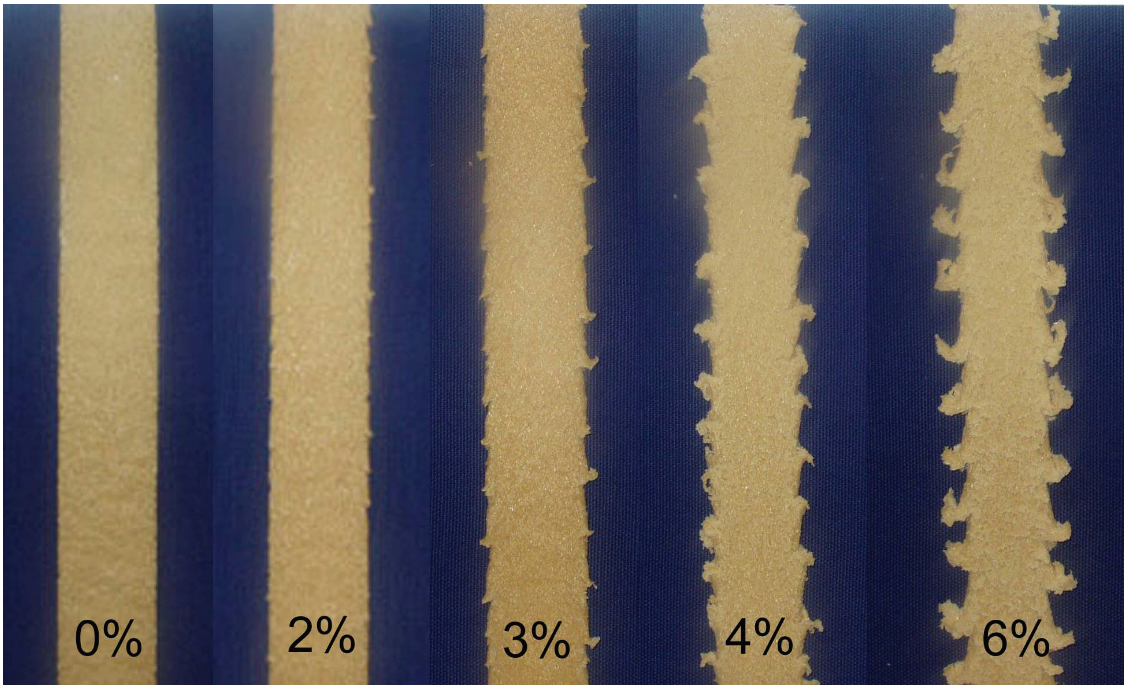

Fig. 4. The extruded composite profiles at different levels of silane solution addition.

Figure 5. Bengtsson and Oksman

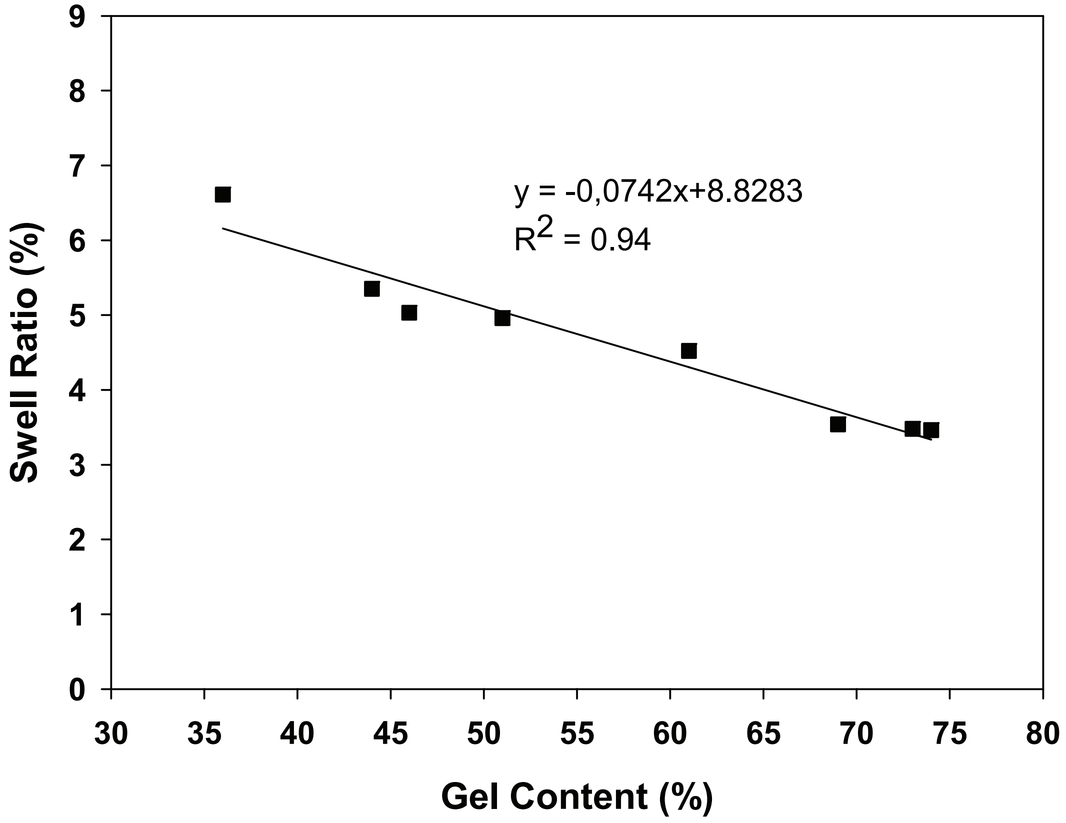

Fig. 5. Swell ratio as a function of gel content in the crosslinked composites.

Figure 6. Bengtsson and Oksman

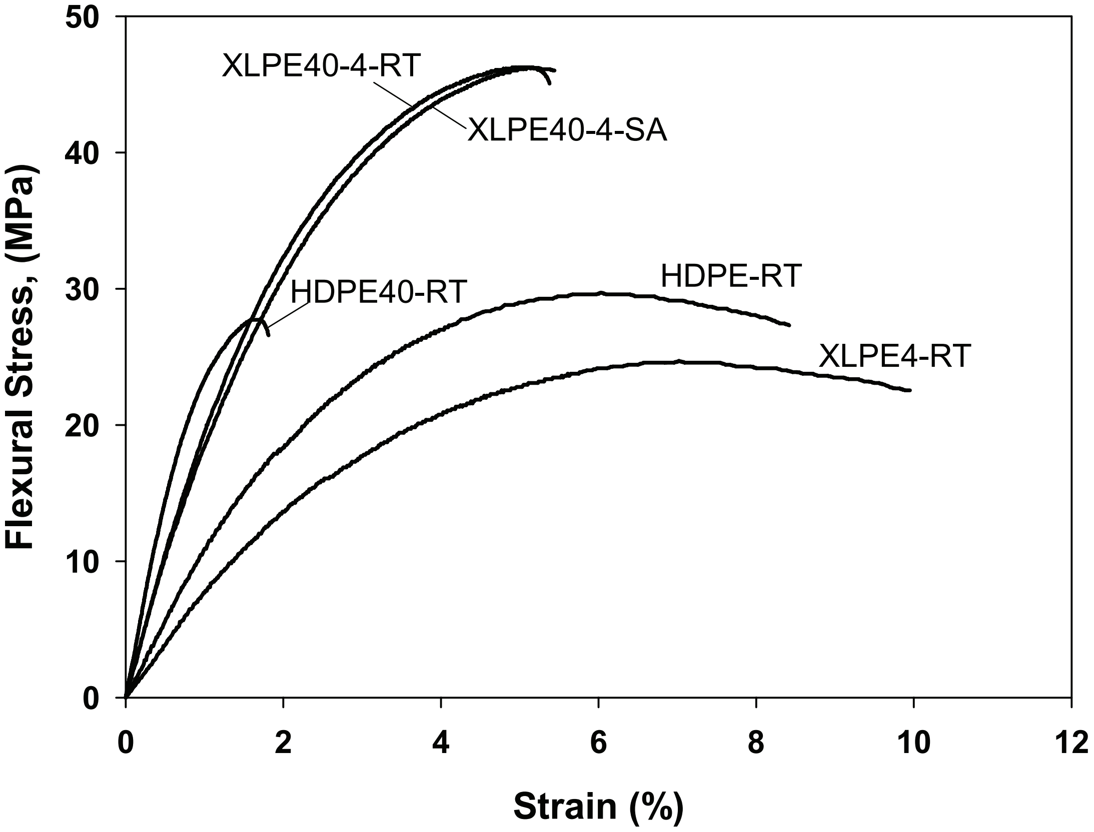

Fig. 6. Typical stress-strain curves for composites and neat plastics. The addition of silane solution in the crosslinked samples is 4 % w/w.

Figure 7. Bengtsson and Oksman

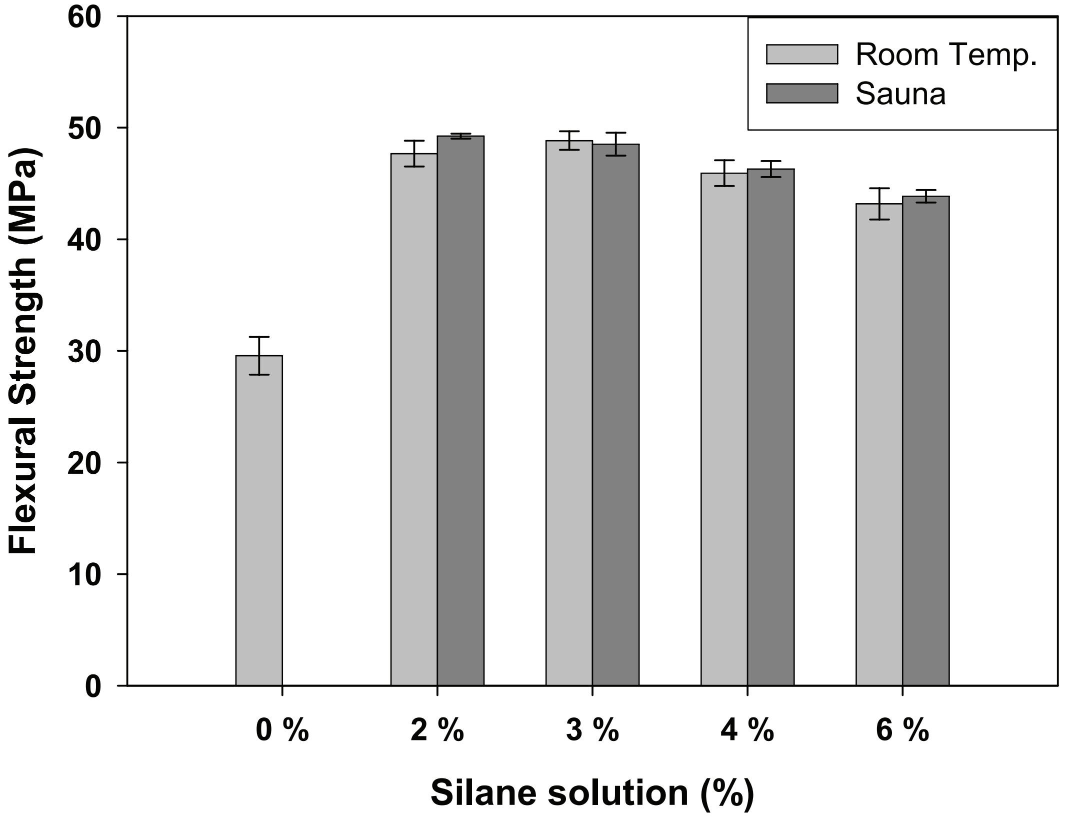

Fig. 7. Average values of flexural strength as a function of added silane solution to the composites.

Figure 8. Bengtsson and Oksman

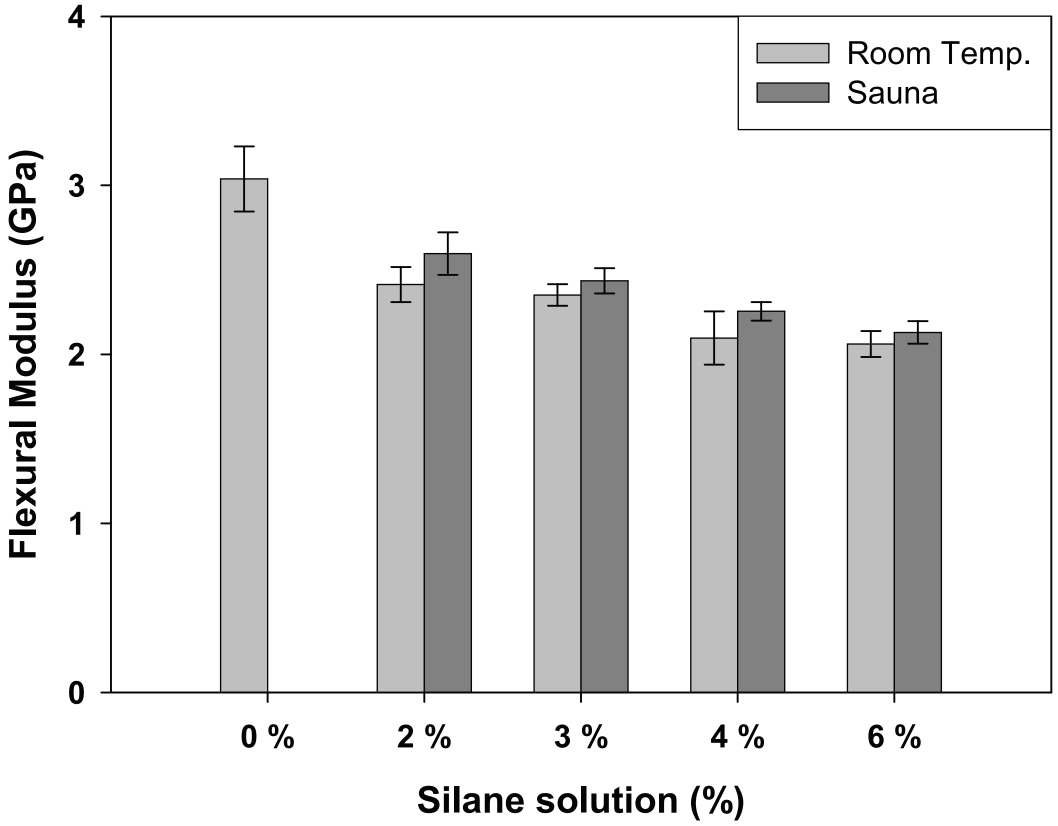

Fig. 8. Average values of flexural modulus as a function of added silane solution to the composites.

Figure 9. Bengtsson and Oksman

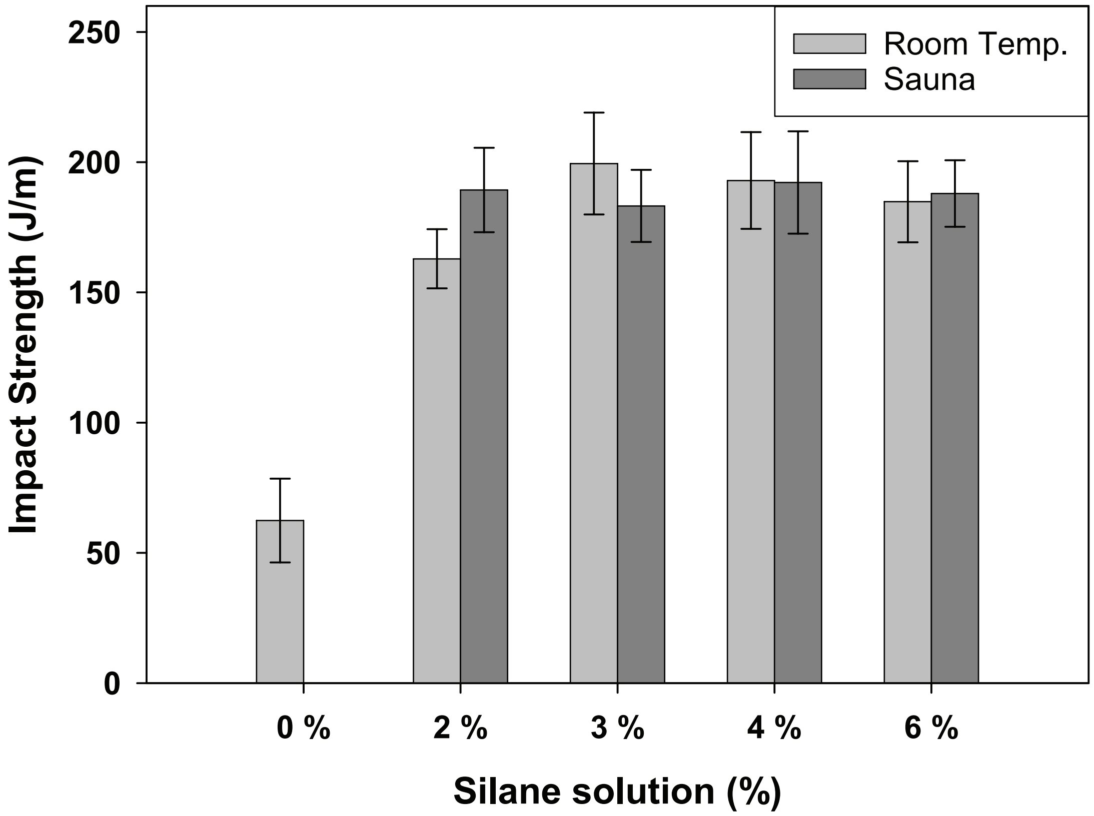

Fig. 9. Average values of impact strength as a function of added silane solution to the composites. The tested composites were un-notched.

Figure 10. Bengtsson and Oksman

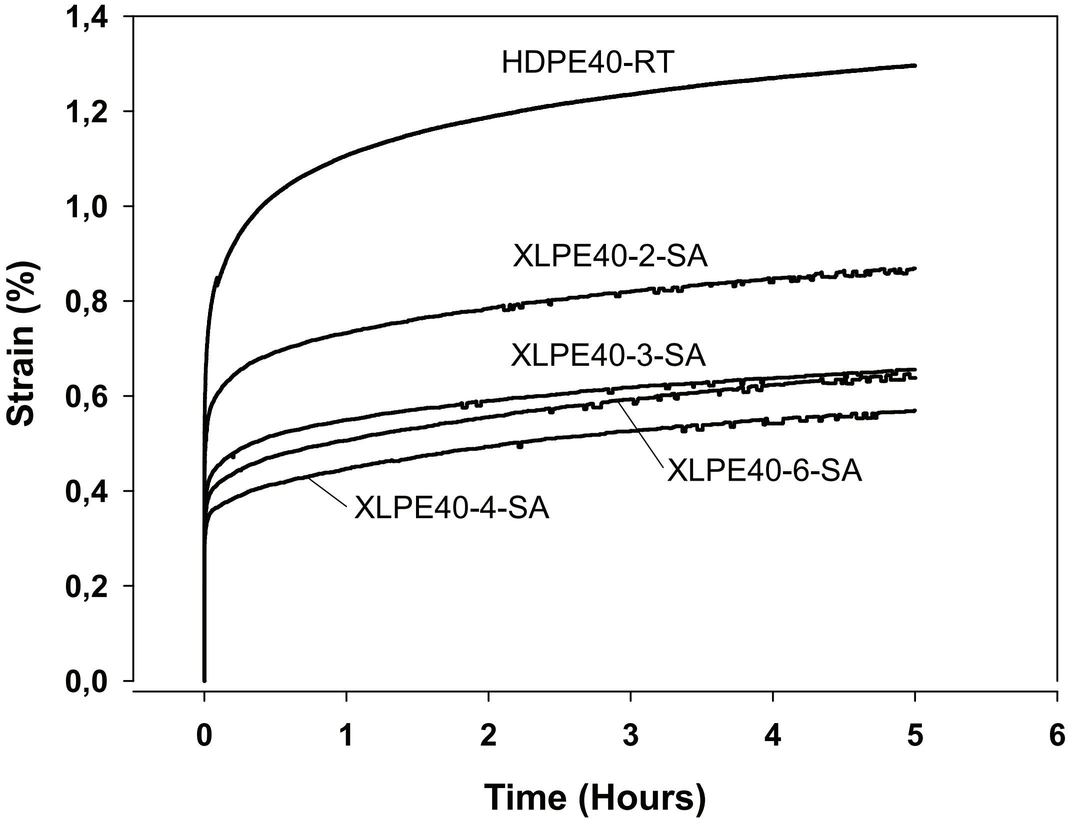

Fig. 10. Creep strain as a function of time during creep experiments at 30 ˚C. The applied static stress was 5 MPa.

Figure 11. Bengtsson and Oksman

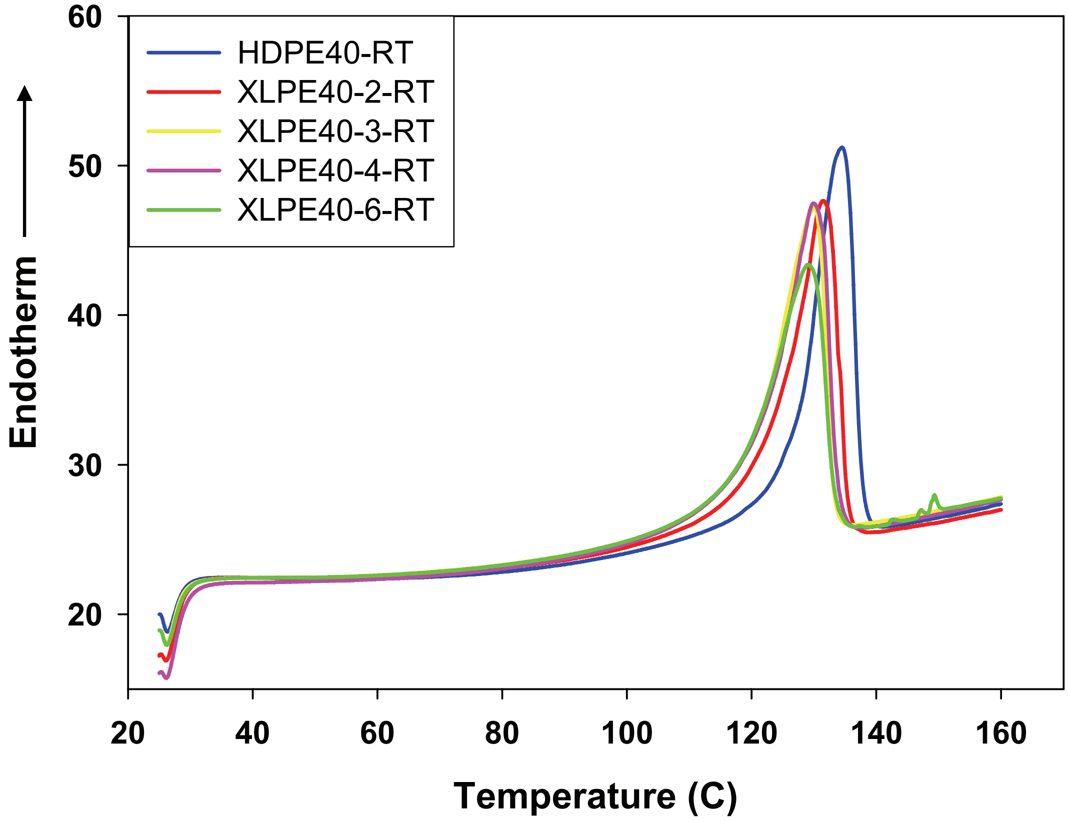

Fig .11. DSC heating thermographs of non-crosslinked and crosslinked composites stored at room temperature.

Figure 12. Bengtsson and Oksman

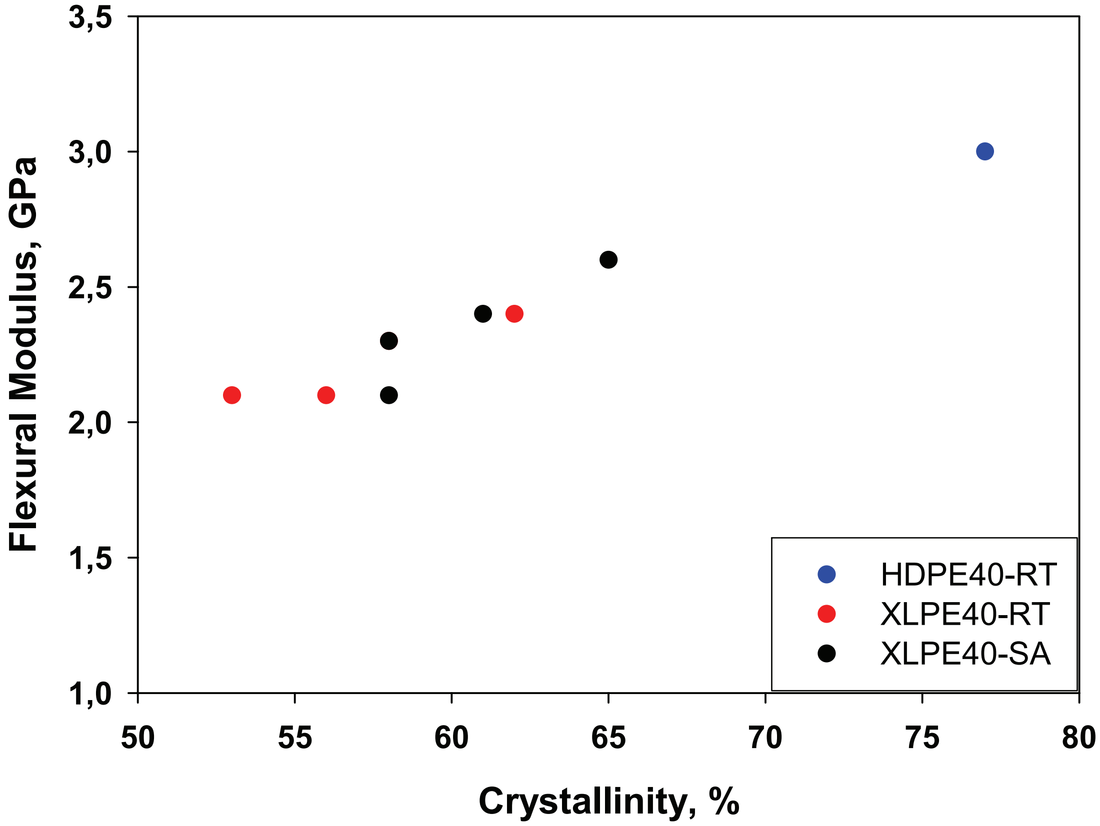

Fig .12. Flexural modulus as a function of crystallinity in the composites.

Table 1.
Processing formulations

Sample code	Weight-%		
	HDPE MG9601	Wood flour	Silane solution[1)]
XLPE-4	96	-	4
XLPE40-2	58	40	2
XLPE40-3	57	40	3
XLPE40-4	56	40	4
XLPE40-6	54	40	6
HDPE	100	-	-
HDPE40	60	40	-

[1)] A solution of vinyltrimethoxy silane and dicumyl peroxide (12:1 w/w)

Table 2.
Gel content and swell ratio of crosslinked composites

Sample code	Gel content (%)	Swell ratio (%)
XLPE40-2-RT	36	6.61
XLPE40-3-RT	44	5.35
XLPE40-4-RT	46	5.03
XLPE40-6-RT	51	4.96
XLPE40-2-SA	61	4.52
XLPE40-3-SA	69	3.53
XLPE40-4-SA	74	3.46
XLPE40-6-SA	73	3.48

Table 3.
Mechanical properties of neat plastics and composites

	Flexural properties			Izod impact
Sample code	Modulus (GPa)	Strength (MPa)	Strain at max (%)	Un-notched (J/m)
HDPE-RT	1.1 ± 0.1	30.5 ± 0.9	6.4 ± 0.4	-
XLPE-4-RT	0.8 ± 0	23.9 ± 0.7	6.5 ± 0.3	-
HDPE40-RT	3.0 ± 0.2	29.6 ± 1.7	1.8 ± 0.2	62.4 ± 16.1
XLPE40-2-RT	2.4 ± 0.1	47.7 ± 1.2	4.3 ± 0.2	162.9 ± 11.3
XLPE40-3-RT	2.3 ± 0.1	48.8 ± 0.8	4.8 ± 0.1	199.5 ± 19.5
XLPE40-4-RT	2.1 ± 0.2	45.9 ± 1.1	4.8 ± 0.4	193.0 ± 18.5
XLPE40-6-RT	2.1 ± 0.1	43.2 ± 1.4	5.2 ± 0.2	184.8 ± 15.6
XLPE40-2-SA	2.6 ± 0.1	49.9 ± 0.2	4.8 ± 0.2	189.3 ± 16.2
XLPE40-3-SA	2.4 ± 0.1	48.5 ± 1.0	5.0 ± 0.1	183.2 ± 13.9
XLPE40-4-SA	2.3 ± 0.1	46.3 ± 0.7	5.0 ± 0.2	192.2 ± 19.6
XLPE40-6-SA	2.1 ± 0.1	43.8 ± 0.6	5.5 ± 0.5	188.0 ± 12.8

Table 4.
Peak melting temperatures (T_m), melting enthalpy (ΔHm), and crystallinity of neat plastics and composites

Sample code	T_m (°C)	ΔHm (J/g)	Crystallinity (%)
HDPE-RT	136.6	188.3	65
XLPE-4-RT	132.2	162.7	56
HDPE40-RT	134.3	222.9	77
XLPE40-2-RT	131.2	179.2	62
XLPE40-3-RT	132.2	168.5	58
XLPE40-4-RT	129.6	162.1	56
XLPE40-6-RT	128.8	153.4	53
XLPE40-2-SA	131.2	188.8	65
XLPE40-3-SA	130.1	177.2	61
XLPE40-4-SA	129.3	169.3	58
XLPE40-6-SA	128.7	168.3	58

Paper IV

Optimization of silane crosslinking technology for use in polyethylene/wood flour composites

Optimization of silane crosslinking technology for use in polyethylene/wood flour composites

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Abstract

The aim of the study was to optimise the silane crosslinking technology for use in polyethylene/wood flour composites. Silane crosslinked wood-polyethylene composites with 0, 2, 3, 4, and 6 % of added silane solution were produced in a one-step compounding process. The composites were stored in a sauna at 90 ºC and at ambient conditions. Gel content and swelling data showed the highest degree of crosslinking in the sauna stored composites. An addition of at least 4 % of silane solution during processing was necessary to fully crosslink the composites in the sauna within 48 hours. The crosslinked composites showed toughness and creep properties superior to those composites to which no silane was added. The flexural strength of the crosslinked composites reached a maximum between 2-3 % w/w of added silane and then decreased with further addition of silane. Moreover, the flexural modulus was lower in the crosslinked samples than in the non-crosslinked. Differential scanning calorimetry measurements of the specimens showed a lower crystallinity in the crosslinked samples than in the non-crosslinked. A linear relationship between the flexural modulus and the crystallinity in the composites was found.

Introduction

Natural and wood fibre plastic composites have made significant gains in popularity over the last decade. The retail value of this industry has been growing nearly 16 % annually since 1998, and is currently valued over $750 million (1). The plastic component in wood plastic composites provides improved resistance to moisture and biological attack over traditional wood composites by encapsulating the wood. (2). The interest in using wood as a reinforcing filler in plastics is due to its low cost, high relative strength and stiffness, low density and the fact that it is a natural resource (3-7). Wood plastic composites are used to replace impregnated wood in many outdoor applications, because of recent regulations of the wood preservative industry. Recent concerns regarding the environmental impact of chromated copper arsenate, the most widely used wood preservative, have resulted in a phase-out of all new uses of this material for residential purposes in the US (8). Wood plastic composites could also replace pure plastics in applications where the increase in stiffness accompanying the addition of wood fibre is an advantage. When proper coupling agents are used to improve fibre-matrix adhesion, wood can also be used as reinforcement to the plastic. The elasticity of wood fibre is approximately forty times greater than that of polyethylene and the overall strength is about twenty times higher (9). There are also environmental reasons for replacing part of the plastic with wood.

Challenges for wood plastic composites include improving the toughness and impact strength, lowering the weight of the composites and improving the long-term material properties. During the past two decades several different methods have been tested in order to improve the toughness of the composites by improving the adhesion between the wood filler and the thermoplastic matrices. One the most commonly used coupling agents is maleated polyethylene or polypropylene (4, 10-14). There have also been some studies on other coupling agents such as isocyanates (15-16) and silanes (15-17). In general, the use of these coupling agents significantly improves the mechanical properties of the composites. In our previous studies we have also seen that silane crosslinking significantly improved the toughness and impact strength of wood plastic composites (18-19). Lowering the weight of wood plastic composites is another challenge for these materials. The density of plastic/wood fibre composites are almost twice that of solid lumber (20). The concept of creating cellular foamed structures has shown to greatly reduce the density of wood plastic composites, and significant improvements in ductility and impact resistance have also been achieved (21). The use of hollow or shaped cross sections can also be used to reduce the weight of wood plastic composites (1). Moreover, improvements in the long-term properties of wood plastic composites are also necessary. Durability during outdoor exposure and long-term load performance are among such properties that have to be improved. Exposure to ultraviolet (UV) radiation and moisture during outdoor use is of particular concern for wood plastic composites (22). Thermoplastics typically perform poorly in long-term loading because linear polymer molecules exhibit a strong time and temperature dependent response. Addition of wood filler to the polymer matrix decreases creep response during loading (18-19, 23), but it is still a problem. Crosslinking of the polymer matrix has shown to be one way of reducing creep during long-term loading (18-19).

Crosslinkable ethylene-vinyl silane copolymers are a commercial product for the global wire and cable market. Silane crosslinking takes place in the presence of trace amounts of water and reactions can be accelerated by incorporating a tin based catalyst. In the first step, methoxyl groups are hydrolysed to hydroxyl groups during the leaving of methanol. Crosslinking takes place in the second step where the hydroxyl groups recombine through a condensation step (24), as shown in Figure 1. Melt grafting of vinyl silane onto polyethylene proceeds in presence of peroxide. At elevated temperature the peroxide first decomposes and creates oxy radicals. These oxy radicals have the potential to abstract hydrogen from the polyethylene polymer but can also attack the vinyl group of the vinyltrimethoxy silane (VTMS) molecule and convert it into radicals. These free radicals either combine with one another or attack another molecule in the same fashion to propagate the free-radical reaction (25). This process results in grafting of vinyl silane onto polyethylene; this is a prerequisite for crosslinking the material. Figure 2a shows the reaction mechanism during peroxide-induced melt grafting of silane onto polyethylene. Melt phase processing of polyolefins is often accompanied by side reactions. These include (26):

a) radical induced crosslinking of the polyolefin
b) radical induced chain scission of the polyolefin
c) shear induced degradation of the polyolefin
d) homo-polymerisation of the monomer

Polyethylenes (HDPE, LDPE, LLDPE) are prone to branching or crosslinking caused by radical-radical combination (26). Figure 2b) shows the reaction mechanism caused by radical induced crosslinking of polyethylene. Some of the crosslinked network in the specimens is thus caused by a radical-radical combination. Radical induced chain scission and shear induced degradation is not as prominent for HDPE as it is for polypropylene (PP) (26). In addition, vinylsilanes (e.g. VTMS) do not readily homo-polymerise (26).

Addition of wood filler during the melt grafting step makes it possible to graft vinyl silane onto both polyethylene and the wood filler. Moreover, there is a possibility of a direct condensation reaction between silanol groups (Si-OH) and hydroxyl groups on wood. This creates a covalent bonding between wood and the silanol group (wood-O-Si), where the vinyl group can be chemically bonded (covalent C-C) or interact through van-der-Waals forces with the polyethylene matrix. In a previous study, we showed that the toughness of silane crosslinked composites was significantly higher than for the non-crosslinked (19). This was explained as a result of improved adhesion between the polyethylene and wood flour phases. Kuan et al. (27) studied silane crosslinked polyethylene-wood flour composites. The wood flour was treated with vinyltrimethoxy silane before compounding with polyethylene. The crosslinking was subsequently initiated by water treatment. Water crosslinked samples exhibited better mechanical properties than the non-crosslinked samples as a result of chemical bonding between both wood and polyethylene. There are also other studies were peroxides have been used to crosslink composites of polyethylene and wood flour / pulp (28-29). The mechanical properties of the crosslinked composites were improved compared to the non-crosslinked. Crosslinking was shown to improve adhesion between polyethylene and wood filler as a result of recombination of radicals formed at the filler surface and polyethylene macro radicals.

In this study, the silane grafting and composite production were carried out simultaneously in a one step process. By doing so, the production of the composites is more economical as well as more industrially friendly. Additionally, by doing the composite manufacturing and silane grafting ourselves, we achieve better control over the degree of crosslinking in the composites. This study is a continuation of an earlier article (19). The aim of this study is to optimize the silane crosslinking technology for use in polyethylene/wood flour composites.

2. Experimental

2.1. Materials

High density polyethylene, HDPE MG9601 (MFI=31 g/10min, 190˚C/5kg), was purchased from Borealis AB (Stenungsund, Sweden). Wood flour from softwood (spruce and pine) was kindly provided by Scandinavian Wood Fiber AB (Orsa, Sweden). According to the supplier, the size of the softwood wood flour was 200-400 µm. The shape of the wood flour was fractured fibre bundles. Vinyltrimethoxy silane 98 % was purchased from Sigma Aldrich (Leirdal, Norway). Dicumyl peroxide, Perkadox BC-FF 99%, was kindly supplied by Akzo Nobel (Gothenburg, Sweden). Throughout this paper the crosslinked samples are sometimes referred to as “XLPE” and the non-crosslinked as “HDPE”. Samples stored at room temperature and in a sauna are abbreviated RT and SA, respectively.

2.2. Processing

The wood flour was dried for 24 hours at 100 ˚C to a moisture content of ~0.3 % (based on dry weight) before processing. Plastic granulates and wood flour were compounded using a Coperion Werner and Pfleiderer ZSK 25 WLE (Stuttgart, Germany) corotating twin-screw extruder. As can be seen in Figure 3, the barrel temperatures were between 165-200 ˚C, the screw speed was 100 rpm, the melt pressure at the die varied between 6-65 bar depending on material blend, and the material output was 6 kg/h. Feeding of the wood flour was performed at temperature zone 4 through a twin-screw side feeder operating at 100 rpm. Silane crosslinked specimens 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 in the samples was 0, 2, 3, 4 and 6 % w/w. Vacuum ventilation at the end of the extruder was used to minimize volatile extractives and un-reacted silane in the final samples. The samples were extruded through a rectangular die with the dimensions of 5 × 30 mm and cooled in ambiently. The samples were subsequently compression moulded (Schwabenthan, Table Press Polystat 200T, Germany) to sheets with a thickness of approximately 3.2 mm. Compression moulding was performed at 190 ˚C with no pressure for 5 min, then 2.5 min with 100 bar pressure and finally 2.5 min with 200 bar pressure. Standard test specimens for mechanical testing were cut from the compression moulded sheets. The processing formulations are shown in Table 1.

2.3. Silane crosslinking

Some of the compression moulded samples were stored for 48 hours at room temperature and the others were stored for 48 hours in a simulated sauna. The storage conditions in the sauna were approximately 100 % RH and 90 ˚C. The sauna stored samples were subsequently dried to their initial weight before testing.

2.4. Gel content

The gel content of the samples was determined using p-xylene extraction according to ASTM standard 2765. 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 crosslinking 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 hours. Extracted specimens were then dried at 150 ˚C until a constant weight was attained and subsequently re-weighed. The gel content of the different blends was determined as the average of two separate analyses. The gel-content was calculated according to the following equation:

Extract % = (weight lost during extraction) / (weight of original specimen-weight of filler)

$$\text{Gel content} = 100 - \text{Extract \%} \tag{1}$$

2.5 Swelling experiments

The swell ratio of crosslinked composites in hot p-xylene for 24 hours was determined in accordance with ASTM standard 2765. Specimens of the crosslinked composites were weighed, immersed in p-xylene at 110 °C for 24 hours, removed, weighed in the swollen state, and dried and reweighed. The swell ratio of the different blends was determined as the average of two separate analyses. The swell ratio was calculated as follows:

$$Swell\ ratio = \left(\frac{W_g - W_d}{W_o - W_e} \right) K + 1 \tag{2}$$

W_g = weight of swollen gel after the immersion period

W_d = weight of dried gel

$W_o = f \times W_s$

f = polymer factor (the ratio of the weight of the polymer in the formulation to the total weight of the formulation).

W_s = weight of specimen being tested

W_e = weight of extract (amount of polymer extracted from the specimen in the test)

K = ratio of the density of the polymer to that of the solvent at the immersion temperature. This ratio is 1.17 for HDPE at 110 °C.

2.6. Mechanical testing

2.6.1 Flexural properties

Flexural properties of the samples were measured on a Tinius Olsen H5K-S UTM equipment (Horsham, PA, USA) in accordance with ASTM D790. The dimensions of the specimens tested were approximately 3.2×12.7×130 mm. The measurements were performed at ambient conditions, i.e. a temperature of 22 ˚C and a relative humidity of approximately 40 %. At least five specimens of each blend were tested.

2.6.2 Creep properties

For the most general case of a linear viscoelastic material the total strain e is the sum of three essentially separate parts: e_1 the immediate elastic deformation, e_2 the delayed elastic deformation and e_3 the Newtonian flow, which is identical to the deformation of a viscous liquid obeying Newton's law of viscosity (30). The magnitudes of e_1, e_2 and e_3 are exactly proportional to the magnitude of the applied stress, so that a creep compliance $J(t)$ can be defined, which is the function of time only:

$$J(t) = \frac{e(t)}{\sigma} = J_1 + J_2 + J_3 \tag{3}$$

where J_1, J_2 and J_3 corresponds to e_1, e_2 and e_3 (30). Crosslinked polymers do not show a J_3 term, and to a very good approximation neither do highly crystalline polymers.

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 1.6×12×30 mm. The applied static stress was fixed at 5 MPa and the temperature was fixed at 30 ˚C.

2.7 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) tests were performed on a DSC-7 (Perkin Elmer, Germany) with samples of approximately 10 mg sealed in aluminium pans. The samples were analysed under nitrogen atmosphere in a temperature range between 25-160 ˚C at a heating range of 10 ˚C/min. The melting temperature and melting enthalpy of the samples were determined. The crystallinity of the samples was calculated according to the following equation:

$$Crystallinity\ (\%) = \frac{\Delta H_{fusion,\ sample}\ (J/g)}{\Delta H_{fusion,\ 100\%\ crystalline\ polyethylene}\ (J/g)} \qquad (4)$$

An enthalpy of fusion of 290 J/g for 100 % crystalline polyethylene was used in the calculation of crystallinity (31). A compensation for the wood flour content was made while calculating the crystallinity in the composites.

3. Results and Discussion

3.1. One-step process

There are several different ways of preparing silane grafted composites. One method is to treat the polyethylene pellets (or wood flour) with a diluted solution of vinyl silane/peroxide and subsequently evaporate the solvent before processing. Disadvantages of this method include use of solvent and that the process is time consuming. Another method would be to pump the vinyl silane/peroxide solution directly into the extruder during processing. This can be done in a two step process where the first step includes silane grafting of neat plastic and the second step incorporation of wood flour. This procedure was used in our first study of silane crosslinked composites (18). In this study, the silane grafting and composite production were carried out simultaneously in a one step process. By doing so, the production of composites is more economical, industrially friendly and also gives the possibility of grafting silane onto both polyethylene and wood flour.

Processing of crosslinked composites was found to be more difficult than processing of the non-crosslinked. Addition of vinyltrimethoxy silane (VTMS) and dicumyl peroxide solution during processing significantly increased the motor load and melt pressure in the extruder. An increase in melt viscosity of polyethylene upon silane grafting was expected. This increase in melt viscosity is due to premature crosslinking but melt viscosity will also increase as a result of interaction between grafted silane groups (26). The increase in melt viscosity and the volatile compounds created during melt grafting reactions contribute to the increased melt pressure. Higher melt pressure occurred with an increased addition of silane solution and reached a maximum at 65 bar when 6 % w/w of silane solution was added. Addition of 2 and 3 % w/w silane solution produced some minor edge tearing of the extruded profiles. The edge-tearing was more significant and the surfaces became rough at an addition of 4 and 6 % w/w silane solution. Difficulties in encapsulating the wood at the surfaces of the profile are believed to be the reason for edge tearing and rougher surfaces of crosslinked composites. The addition of lubricant during processing might eliminate these problems. To avoid the risk of interference between the silane/peroxide solution and the lubricant, no lubricant was used in this study.

3.2. Degree of crosslinking

The degree of crosslinking in the composites was determined by gel content and swell ratio measurements. The gel content of the crosslinked composites was determined using p-xylene extraction in accordance with ASTM standard 2765. Crosslinked polyethylene is insoluble in boiling p-xylene while the non-crosslinked part is soluble. The gel content can thus be determined gravimetrically from the extracted samples. Storage at environments with different humidity levels i.e. in a simulated sauna at 90 ˚C, ~ 100 % RH and at room temperature, affected the degree of crosslinking in the samples. As can be seen in Figure 1, the first step in the crosslinking reaction is hydrolysis of the methoxyl groups to silanol groups. Water is responsible for the hydrolysis of the methoxyl groups. A higher humidity level would thus be expected to create a higher degree of crosslinking in the samples. As can be seen in Table 2, storage in a high humidity sauna generated a higher degree of crosslinking in the composites than storage at room temperature. In a previous study it was shown that storage of silane modified composites at room temperature did not significantly affect the gel content in the composites (19). The degree of crosslinking in the composites stored at room temperature is thus believed to correspond to the crosslinking that takes place during processing. A higher gel content with an increased addition of silane solution was found in the composites stored at room temperature. This shows that a higher level of silane addition during processing increases the crosslinking that takes place during processing. Moreover, storage of the composites in a sauna significantly increased the gel content in the composites. In the composite to which 2 % w/w of silane solution was added during processing, the gel content after storage in a sauna was lower (61 %) than composites with a higher level of silane addition. The sauna stored composites with 3, 4 and 6 % w/w of added silane during processing all had a gel content in the range between 69 to 74 %. Earlier studies have shown that the maximum gel content during silane crosslinking is in the range between 75-80 % (19, 24). An addition of 4 % w/w or more of the silane solution during processing thus seem necessary to fully crosslink the composites in a sauna within 48 hours.

The swell ratio of crosslinked composites in hot p-xylene for 24 hours was determined in accordance with ASTM standard 2765. The swell ratio of the crosslinked composites was determined in order to study the correlation between gel content and network density. In Figure 4, the swell ratio as a function of gel content is shown. As can be seen in the figure, there is a semi-linear relationship between swell ratio and gel content. A higher gel content is thus evidence of an increased network density. The network density is thus highest in the sauna stored composites to which 4 % w/w or more of silane solution was added during processing. The data from the swelling study is summarised in Table 3.

3.3 Mechanical properties

3.3.1. Flexural properties

All the mechanical data from the flexural testing are summarised in Table 4. As can be seen in the table, the flexural strength of neat HDPE was higher than in neat XLPE. Differential scanning calorimetry analysis (see section 3.4) showed a lower crystallinity of neat XLPE than in neat HDPE. The lower crystallinity in the crosslinked samples could explain their lower strength. It is also possible that there might be some silane in the samples that is blended into the system without reacting. The un-reacted silane could act as a plasticizer and lower the strength of the neat XLPE samples compared to neat HDPE. In Figure 5, the average values of flexural strength as a function of silane addition to the composites are shown. In contrast to the neat plastics, the crosslinked composites showed flexural strength superior to the composites to which no silane was added. The improved strength in the crosslinked composites is most likely caused by improved adhesion between wood and polyethylene. Therefore, even though the crystallinity of the polyethylene matrix was lower in the crosslinked samples than in the non-crosslinked, and there might be un-reacted silane plasticizing the composites, the flexural strength was significantly higher in the crosslinked composites than in the non-crosslinked composites. Improved adhesion between wood and plastic makes it possible for stress transfer from the weaker plastic matrix to the stronger wood fibre during loading, thereby improving the strength of the crosslinked composites. The improved adhesion could be due to covalent bonding between wood and 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. Without interfacial adhesion, the strength would decrease upon addition of wood flour as is the case for the non-crosslinked composites. The flexural strength in the crosslinked composites reached a maximum between 2-3 % w/w of added silane and then decreased with further addition of silane. The lower strength in the crosslinked composites with 4 and 6 % w/w of added silane is believed to be caused by lower crystallinity in those samples. The potential plasticizing effect of un-reacted silane would also be more significant at a higher level of silane addition. The flexural strength in crosslinked composites stored at room temperature did not differ much from the ones stored in a sauna. This indicates that the reactions responsible for improving the adhesion between wood and polyethylene mainly takes place during the higher temperature used under processing. The improved adhesion between wood and polyethylene in the crosslinked composites is also believed to explain the superior flexural strain before break. All the crosslinked composites could be stretched more than 5 % and most of the samples did not break at all during the experiment. The non-crosslinked, on the other hand, all broke during the experiment and usually at a strain level less than 3 %. Without interfacial adhesion, the gap between the wood and polyethylene phases, provides an area of weakness which easily propagates a crack through the material. As can be seen in Figure 6, the flexural modulus of the silane crosslinked samples is lower than for the non-crosslinked one. Independent of storage conditions (i.e. at room temperature or in a sauna), the modulus also decrease with an increased amount of added silane. Earlier work on silane crosslinked polyethylene-wood flour composites did not show a decrease in modulus upon crosslinking (27). Kuan et al. (27) treated wood flour with 2 phr (parts per hundred parts of resin) of vinyltrimethoxy silane before compounding with polyethylene in an extruder and thereafter injection moulding. In their study the water crosslinked composites showed higher flexural modulus than the non-crosslinked. In Figure 7, the flexural modulus as a function of the crystallinity in the composites is plotted. There is an almost linear relationship between the flexural modulus and the crystallinity in the composites. The decrease in crystallinity with increased amount of added silane to the composites is thus believed to explain the lowering in modulus. On the other hand, one should not exclude the possibility of a plasticizing effect of un-reacted silane which could also lower the modulus in crosslinked samples.

3.3.2. Short-term creep

In Figure 8, the results from the short-term creep test of non-crosslinked and crosslinked (stored in a sauna) composites are shown. The creep response in the crosslinked composites is significantly lower than in the non-crosslinked composite. A lower creep in the crosslinked composites compared to the non-crosslinked composites can be related to a reduced viscous flow of the matrix due to crosslinking as well as improved adhesion between the polyethylene matrix and wood flour. As can be seen in the figure, the creep response in the crosslinked composites decreased with increased amount of added silane. However, the composite with 6 % w/w of added silane showed a slightly higher creep response than in the composite with 4 % w/w of added silane. There is a good correlation between the creep response and the degree of crosslinking in the composites. A higher degree of crosslinking (i.e. higher gel content) lowers the creep response in the composites. One would expect the creep response in the composites with 4 and 6 % w/w of added silane to show more similar creep behaviour since the gel content in these composites was equivalent. In an earlier study of silane crosslinked composites, it was also shown that a higher degree of crosslinking lowered the creep response (19). In that study, crosslinked composites stored in a sauna showed lower creep response than composites stored at room temperature.

3.4 Crystallinity

Differential scanning calorimetry (DSC) analyses were used to determine the crystallinity in the samples. The DSC measurements were performed to study if the crosslinking affected the crystallinity and thereby the mechanical properties in the samples. Figure 9 shows the DSC thermographs of non-crosslinked and crosslinked composites stored at room temperature. As can be seen in the figure, the melting endotherm (ΔH_{fusion}) is lower in the crosslinked samples compared to the non-crosslinked one. This is evidence of a lower degree of crystallinity in the crosslinked samples. The crystallinity also decreases with increased amount of added silane to the samples during processing. The melting peak temperature of the crosslinked composites is also slightly lower than in the non-crosslinked one. In Table 5, the crystallinity and the melting peak temperatures from the DSC analyses are summarised. Crosslinked composites stored in a sauna also showed lower crystallinity than the non-crosslinked composite stored at room temperature. Moreover, the crosslinked composites stored in a sauna showed a slightly higher crystallinity than in the crosslinked composites stored at room temperature. The slightly higher crystallinity in crosslinked composites stored in a sauna can be related to some re-crystallization taking place during storage in a sauna at 90 ˚C. DSC analysis of the neat plastics also showed the same trend, with a lower crystallinity (56 %) in XLPE-4-RT compared to 65 % in HDPE-RT. Since silane crosslinking mainly takes place in the solid state, the crystalline phase should not undergo considerable changes, rather the crosslinking takes place only in the amorphous phase. However, as was shown in Table 2 (gel content) the crosslinking reaction is initiated already during extrusion. This initial crosslinking can be due to silane crosslinking but might also be due to side reactions as was described in the introduction section. The crosslinked polyethylene forms a network structure. The network structure makes the macromolecules chain less flexible, so the crystallization melt peak becomes lower and crystallization more difficult. A higher level of silane addition during processing increased the degree of crosslinking in the composites. This explains the decrease in crystallinity with increased amount of added silane to the composites. A lower crystallinity in silane crosslinked specimens has also been reported by other authors (31-32).

Conclusions

Silane crosslinked composites with different amount of silane were produced in a one step process. Processing of the crosslinked composites was found to be more difficult than processing of the non-crosslinked. At a higher level of silane addition, edge-tearing became a problem and the extruded profiles got a rougher surface. The crosslinking was shown to be initiated already during the compounding process in the extruder. Storage in a high humidity sauna at 90 ˚C generated a higher degree of crosslinking in the composites than storage at room temperature. An addition of at least 4 % w/w silane solution during processing was necessary to fully crosslink the composites in a sauna within 48 hours. Swelling experiment in hot p-xylene showed an almost linear relationship between swell ratio and gel content. The network density was highest in the sauna stored composites to which 4 % w/w or more of silane solution was added during processing. The flexural strength and elongation at break was significantly higher in the silane crosslinked composites than in the non-crosslinked one. The improved toughness in the crosslinked composites is most likely caused by improved adhesion between the wood and polyethylene phases. The flexural strength in the crosslinked composites reached a maximum between 2-3 % w/w of added silane and then decreased with further addition of silane. The flexural modulus was lower in the crosslinked composites than in the non-crosslinked ones. Moreover, short-term creep analysis showed that the creep response in crosslinked composites was significantly lower than in the non-crosslinked composite. The lower creep in the crosslinked composites was related to a reduced viscous flow due to crosslinking, as well as to improved adhesion between the polyethylene matrix and wood flour. Moreover, there was a good correlation between the creep response and the degree of crosslinking in the composites. A higher degree of crosslinking in the composites lowered the creep response. Differential scanning calorimetry measurements of the specimens showed that the crystallinity of the polyethylene matrix was lower in the crosslinked samples than in the non-crosslinked ones. An increased amount of added silane was also found to decrease the crystallinity in the composites. The decrease in crystallinity was explained as a result of the initial crosslinking that took place during the processing, which made the macromolecules less flexible and crystallization more difficult. An almost linear relationship between the flexural modulus and the crystallinity in the composites was found. The decrease in crystallinity with increased amount of added silane was thus believed to explain the lowering in modulus and strength. On the other hand, one should not exclude the possibility of a plasticizing effect of un-reacted silane which could also lower the modulus and strength in crosslinked samples.

This study provides a basis for proposing, that an addition of 4 % w/w or more of silane solution during processing is necessary to fully crosslink the composites in a sauna (90 °C, 100 % RH) within 48 hours. Considering the flexural strength and stiffness of the composites, an optimum addition of silane solution is in the range of 2-3 % w/w. On the other hand, if a low creep response in the composites is of first priority an addition 4 % w/w of silane solution is preferable.

Acknowledgement

The financial support of the Research Council of Norway is gratefully acknowledged. We would also like to thank Scandinavian Wood Fiber AB for supplying wood fibres.

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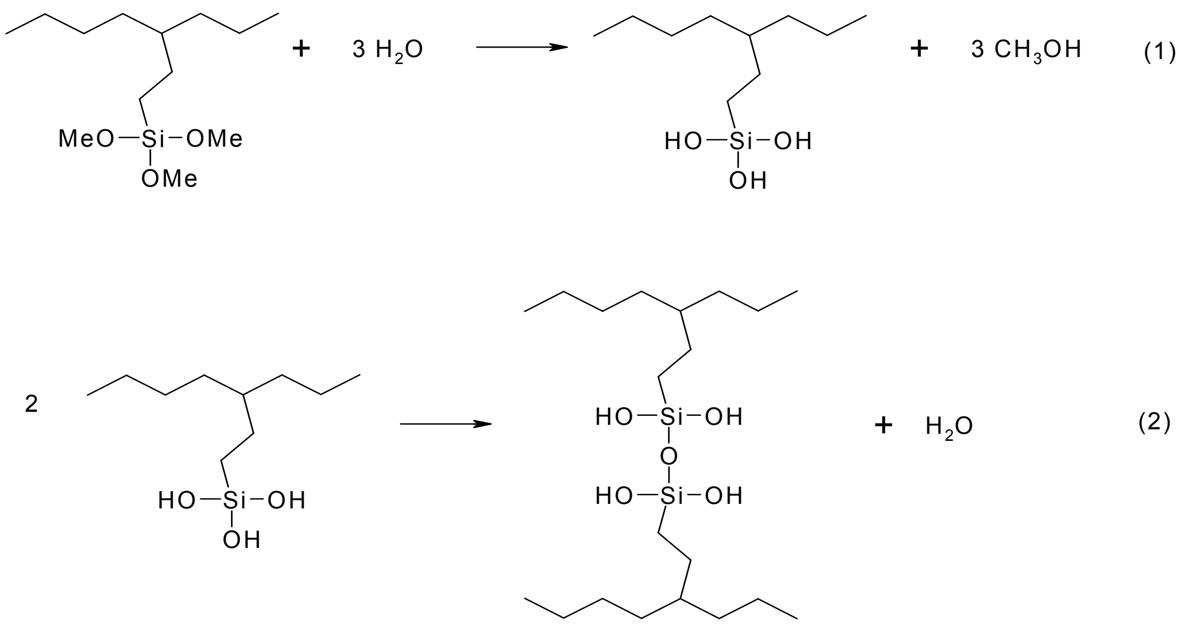

Figure 1. *The hydrolysis step (1) and condensation step (2) during silane crosslinking.*

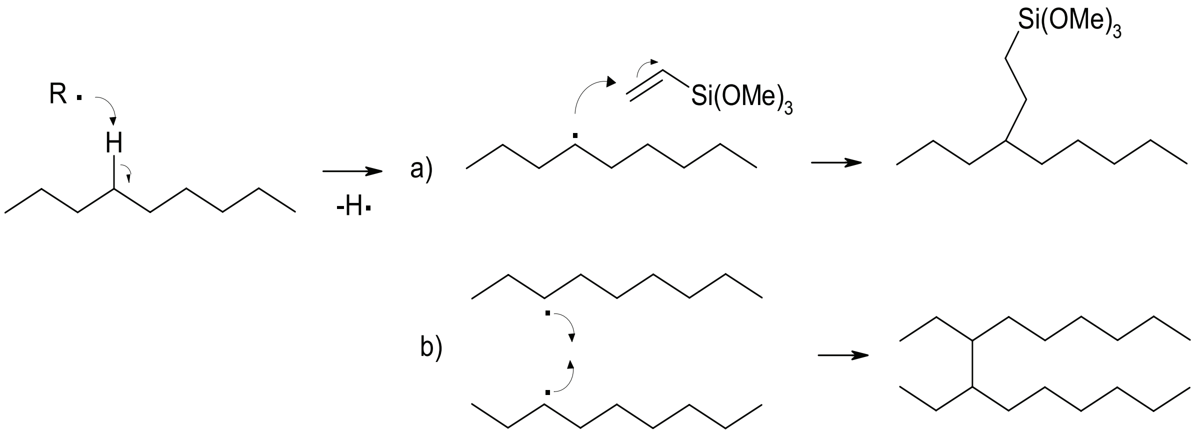

Figure 2. *The reaction mechanism during a) peroxide induced melt grafting of silane onto polyethylene, b) radical induced crosslinking of polyethylene*

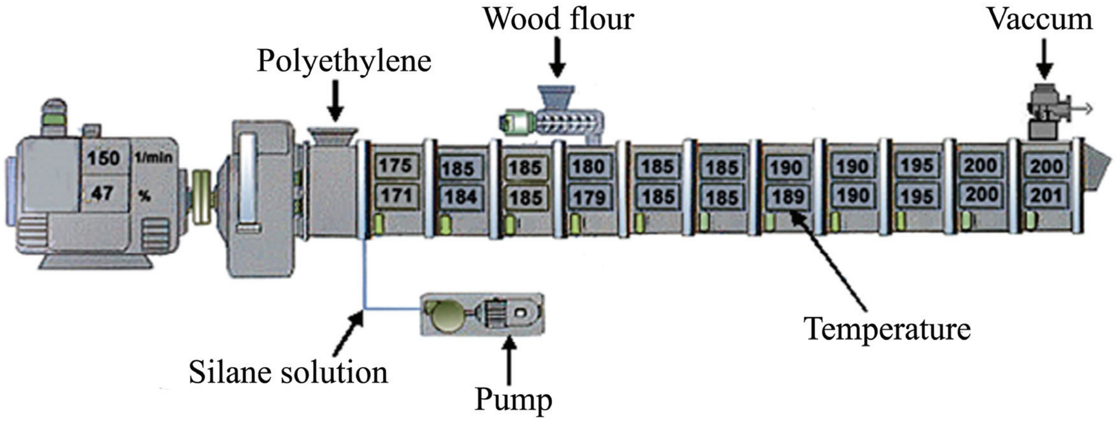

Figure 3. *Extruder setup during processing.*

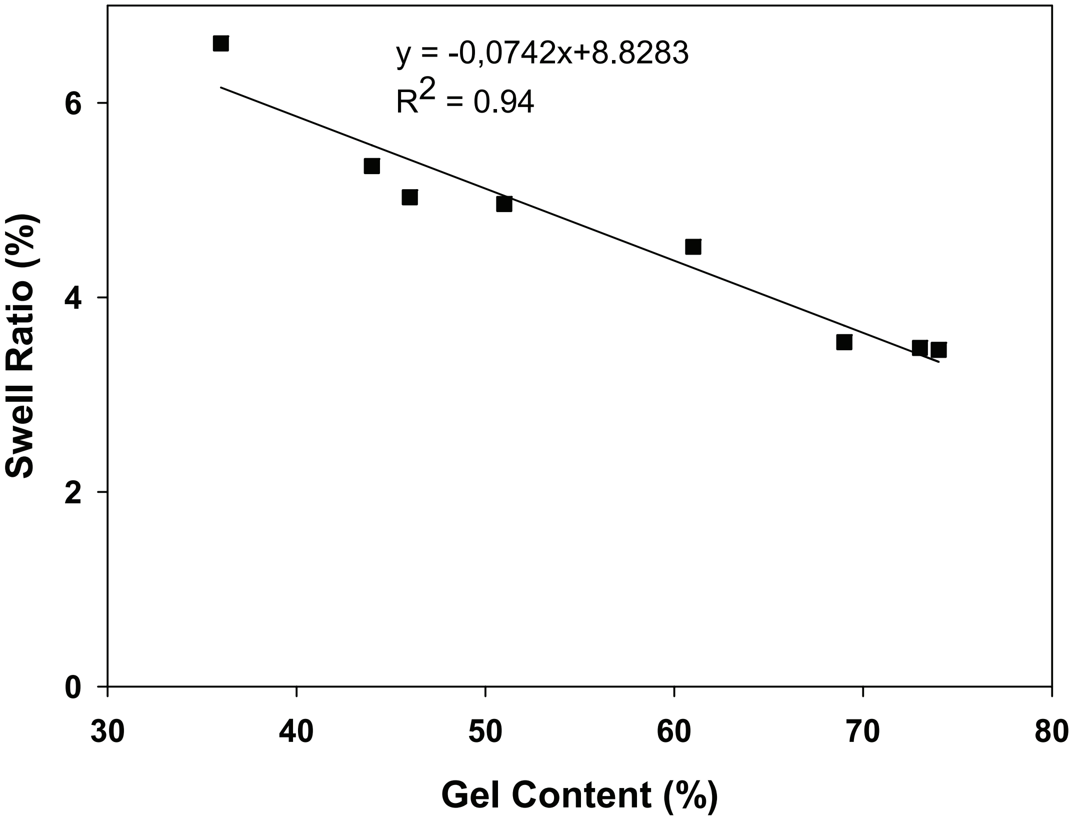

Figure 4. *Swell ratio as a function of gel content in the crosslinked composites.*

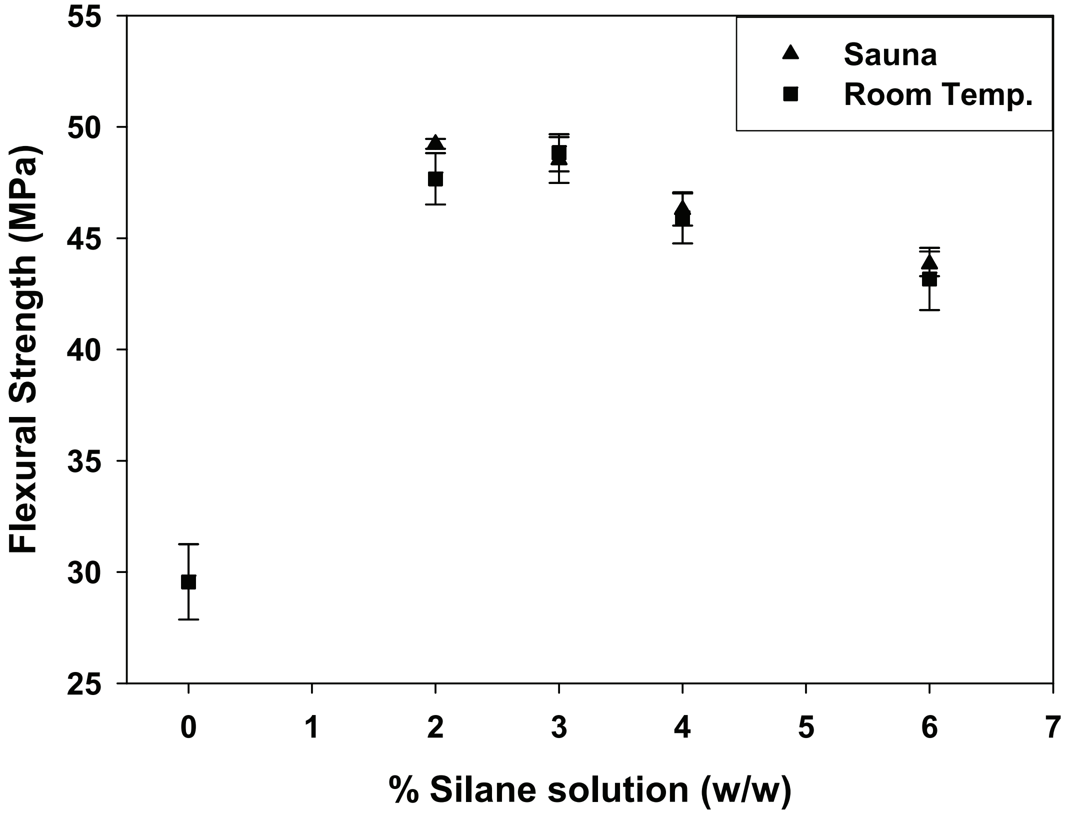

Figure 5. *Average values of flexural strength as a function of silane addition to the composites.*

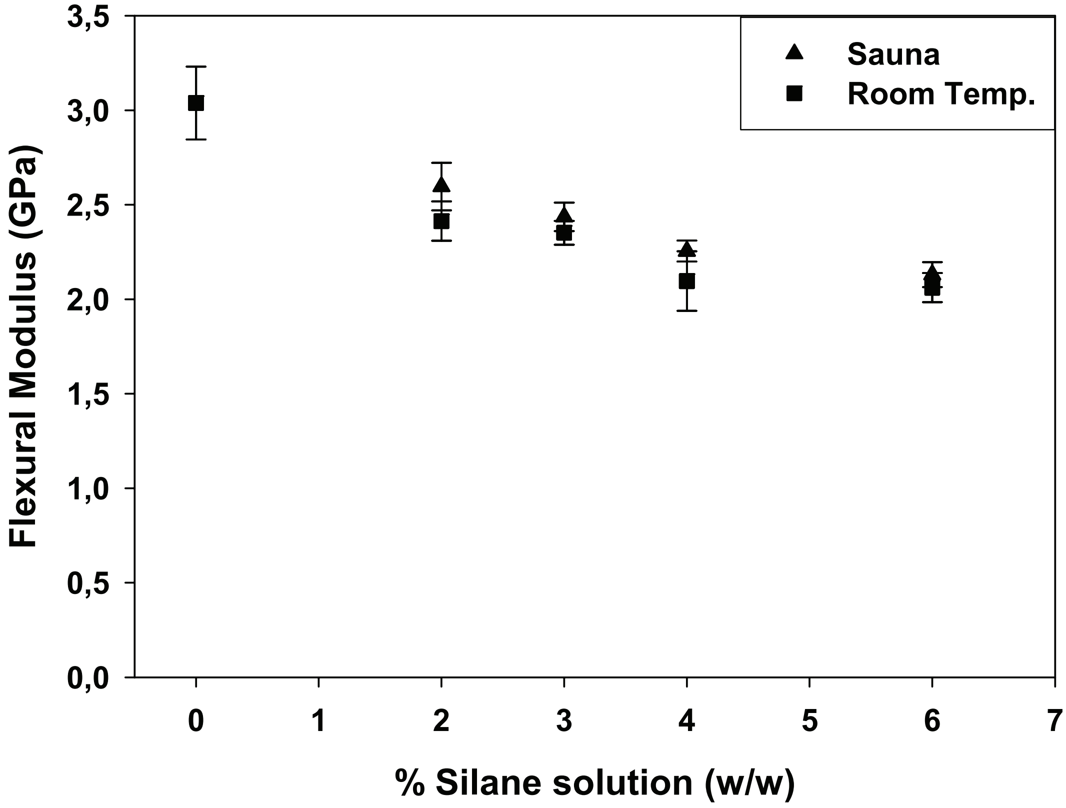

Figure 6. *Average values of flexural modulus as a function of silane addition to the composites.*

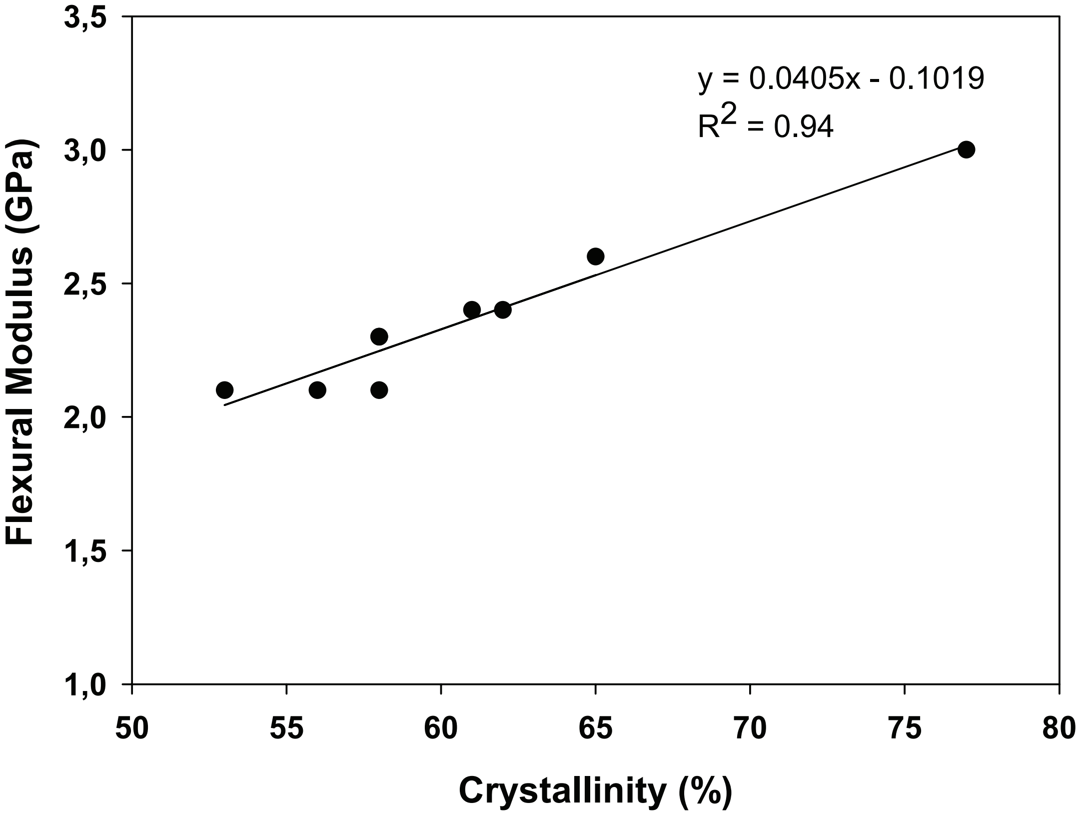

Figure 7. *Flexural modulus as a function of crystallinity in the composites.*

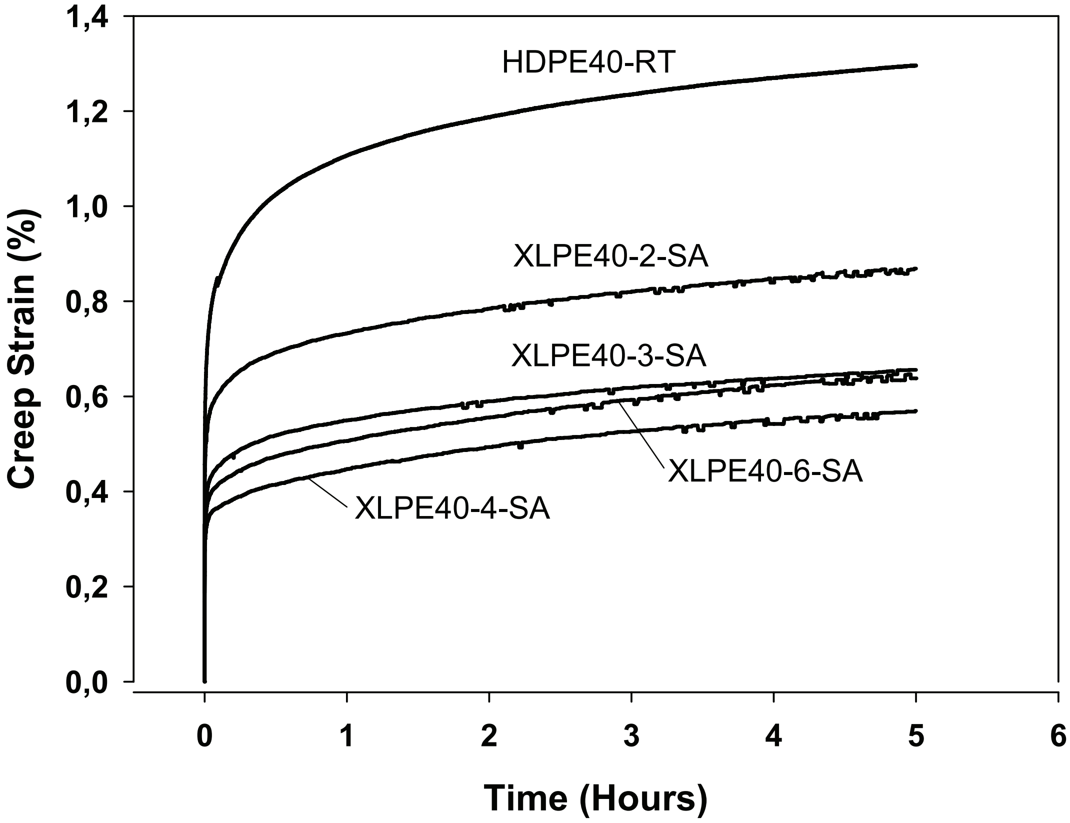

Figure 8. *Creep strain as a function of time during creep experiments at 30 ˚C. The applied static stress was 5 MPa.*

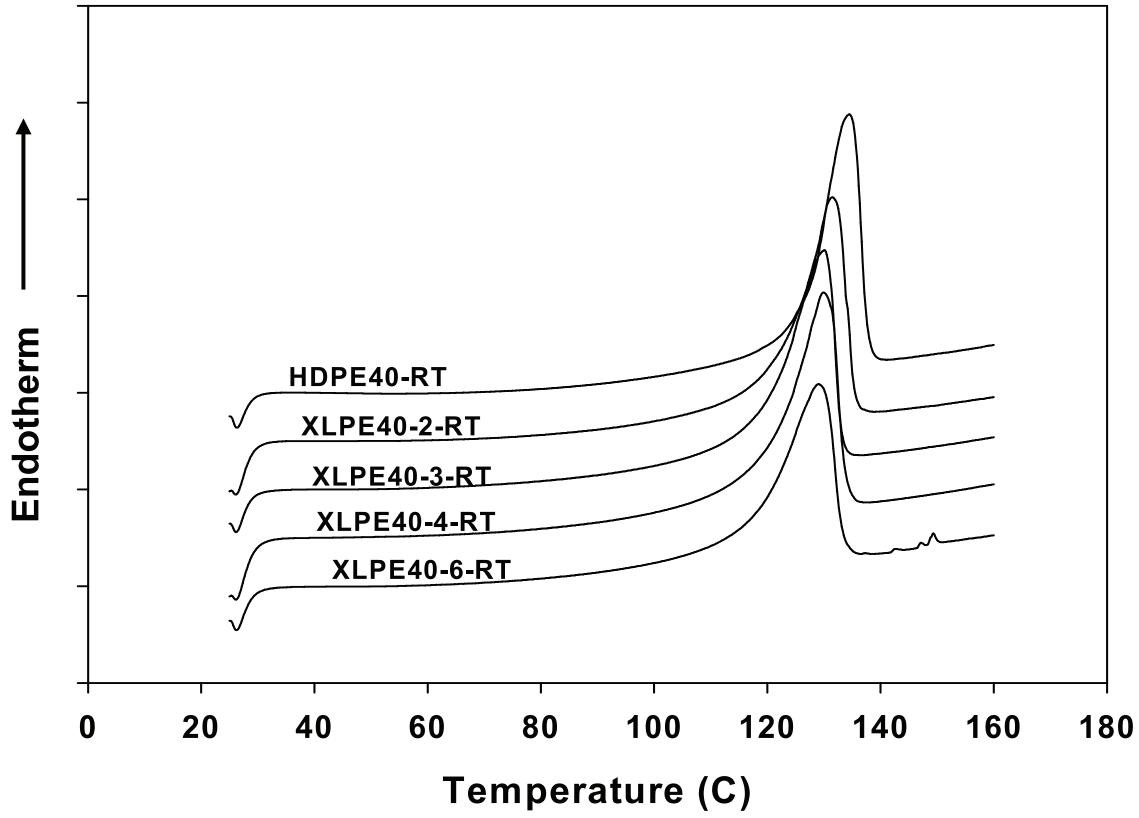

Figure 9. *DSC heating thermographs of non-crosslinked and crosslinked composites stored at room temperature.*

Table 1.
Processing formulations

Sample code	Weight-% HDPE MG9601	Weight-% Wood flour	Weight-% VTMS[1)]
XLPE-4	96	-	4
XLPE40-2	58	40	2
XLPE40-3	57	40	3
XLPE40-4	56	40	4
XLPE40-6	54	40	6
HDPE	100	-	-
HDPE40	60	40	-

[1)] A solution of vinyltrimethoxy silane and dicumyl peroxide (12:1 w/w)

Table 2.
Gel content of crosslinked composites

Sample code	Gel content (%)	
	Room Temp.	Sauna
XLPE40-2	36	61
XLPE40-3	44	69
XLPE40-4	46	74
XLPE40-6	51	73

Table 3.
Swell ratio of the crosslinked composites

	Swell ratio (%)	
Sample code	Room Temp.	Sauna
XLPE40-2	6.61	4.52
XLPE40-3	5.35	3.53
XLPE40-4	5.03	3.46
XLPE40-6	4.96	3.48

Table 4.
Mechanical properties of neat plastics and composites

Sample code	Flexural properties Modulus (GPa)	Strength (MPa)	Strain at max (%)
HDPE-RT	1.1 ± 0.1	30.5 ± 0.9	6.4 ± 0.4
XLPE-4-RT	0.8 ± 0	23.9 ± 0.7	6.5 ± 0.3
HDPE40-RT	3.0 ± 0.2	29.6 ± 1.7	1.8 ± 0.2
XLPE40-2-RT	2.4 ± 0.1	47.7 ± 1.2	4.3 ± 0.2
XLPE40-3-RT	2.3 ± 0.1	48.8 ± 0.8	4.8 ± 0.1
XLPE40-4-RT	2.1 ± 0.2	45.9 ± 1.1	4.8 ± 0.4
XLPE40-6-RT	2.1 ± 0.1	43.2 ± 1.4	5.2 ± 0.2
XLPE40-2-SA	2.6 ± 0.1	49.9 ± 0.2	4.8 ± 0.2
XLPE40-3-SA	2.4 ± 0.1	48.5 ± 1.0	5.0 ± 0.1
XLPE40-4-SA	2.3 ± 0.1	46.3 ± 0.7	5.0 ± 0.2
XLPE40-6-SA	2.1 ± 0.1	43.8 ± 0.6	5.5 ± 0.5

Table 5.
Peak melting temperatures (T_m) and crystallinity of the neat plastics and composites

Sample code	T_m (°C)	Crystallinity (%)
HDPE-RT	136.6	65
XLPE-4-RT	132.2	56
HDPE40-RT	134.3	77
XLPE40-2-RT	131.2	62
XLPE40-3-RT	132.2	58
XLPE40-4-RT	129.6	56
XLPE40-6-RT	128.8	53
XLPE40-2-SA	131.2	65
XLPE40-3-SA	130.1	61
XLPE40-4-SA	129.3	58
XLPE40-6-SA	128.7	58

Paper V

Profile extrusion and mechanical properties of crosslinked wood-thermoplastic composites

Profile Extrusion and Mechanical Properties of Crosslinked Wood-Thermoplastic Composites

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Introduction

In recent years, the use of wood as reinforcing filler in plastics has received considerable attention. Wood provides advantages over conventional reinforcing materials such as low cost, abundancy, renewability, low specific gravity, and high specific strength and stiffness (1-3). Wood-plastic composites are an alternative material for pressure treated wood. Pressure treatment of wood with chemical preservatives is necessary to retard biological decay and insect attack (4). Chromated copper arsenate (CCA) is currently the most widely used wood preservative due to its excellent fungicidal and insecticidal properties (5). However, the impact this and other chemicals may have on the environment is cause for concern. In addition, the treatments do little to resist the dimensional changes accompanying moisture absorption (4). The plastic component in wood-plastic composites encapsulates the wood and thereby improves the durability against moisture and biological attack (6). Moreover, wood plastic composites can be an alternative material for unfilled plastics. Wood-plastic composites can be readily processed in conventional processing equipment for plastics, such as extrusion and injection moulding. Addition of wood to the plastic matrix increases the stiffness of the material. When proper interfacial adhesion between the wood and the plastic matrix is achieved, the strength of the composite is also higher than for unfilled plastic.

In the last decade, there has been a lot of research in improving compatibility between the hydrophilic wood filler and the hydrophobic plastic matrix in wood-plastic composites. Stress transfer from the weaker plastic matrix to the stronger wood fibres plays an important role in determining the mechanical properties of the composites (7). Many authors have published work on different types of coupling agents. One of the most commonly used coupling agents is maleic anhydride grafted polyolefins (7-11). There have also been some studies on other types of coupling agents, such as silanes (12-14) and isocyanates (12-13). An elastomeric copolymer, maleated styrene-(ethylene-co-butylene)-styrene (SEBS-g-MA) has also been reported to improve both the tensile strength and the impact strength of wood-plastic composites (15). In our previous studies, we have also shown that silane crosslinking improved the toughness and impact strength of wood-plastic composites through improved bonding at the wood-matrix interface (16-18).

According to Smith and Wolcott (4), challenges for wood-plastic composites for use in structural applications include develop structural design values, lower product weight, and improve long-term load performance. Existing wood-plastic composite products are typically used in applications where they are not critical structural elements (19). For this reason, establishment of nominal design values for structural applications of these products has not been a high priority. As wood plastic composite products extends to include more structural applications, it is necessary to determine appropriate structural design values. The density of wood-plastic composites is almost twice that of solid wood (20). The weight of wood-plastic composites can be reduced by foaming of the wood-plastic composite (20-21). Another way to reduce the weight of wood-plastic products is the use of hollow or shaped cross-sections (4). Long-term material properties of wood-plastic composites also need improvements. Even though the durability of wood-plastic composites during outdoor exposure is superior to that of untreated wood, it is still a problem. Stark et al. (22) showed that wood-plastic composites experience a colour change and loss in mechanical properties with accelerated weathering. Exposure to ultraviolet (UV) radiation and moisture during outdoor use is of particular concern for wood plastic composites (22). Furthermore, long-term load performance of wood-plastic composites also needs improvements. Wood-plastic composites experience a time-dependent behaviour when subjected to constant load. Creep is the increase in deformation over time when subjected to a sustained load (23). Crosslinking of the polymer matrix is one way of reducing the creep during long-term loading of wood-plastic composites (16-18).

Several techniques have been developed to obtain crosslinked polyethylene: peroxide crosslinking, irradiation techniques and silane crosslinking. However, both peroxide and irradiation crosslinking techniques involve high investment costs (24). Other drawbacks are the risk of pre-curing and high production cost during peroxide crosslinking and the thickness limitation in radiation crosslinking (24). The silane crosslinking 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 crosslinked after the processing steps. Grafting of vinyl silanes onto the polyethylene backbone is initiated by peroxide. The peroxide molecule dissociates by heat and forms radicals. The radicals have the potential to abstract hydrogen from the polyethylene polymer but can also attack the vinyl group of the vinyltrimethoxy silane molecule and convert it into radicals. These free radicals either combine with one another or attack another molecule in the same fashion to propagate the free-radical reaction (25). This process results in grafting of vinyltrimethoxy silane onto polyethylene; this is a prerequisite for crosslinking the material. *Fig. 1a* shows the reaction mechanism during peroxide-induced melt grafting of vinyltrimethoxy silane onto polyethylene. The most prominent side reaction during melt grafting of vinyltrimethoxy silane onto high density polyethylene is crosslinking or branching caused by radical-radical combination (26). *Fig. 1b)* shows the reaction mechanism caused by radical induced crosslinking of polyethylene. Some of the crosslinked network in the specimens is thus caused by a radical-radical combination. The silane crosslinking reaction takes place in the presence of trace amounts of water. The silane crosslinking reaction proceeds over two steps as is shown in *Fig. 2*. In the first step the methoxyl groups are hydrolysed to hydroxyl groups during leaving of methanol. The crosslinking takes place in the second step where the hydroxyl groups recombine through a condensation step (27).

Preparation of silane grafted composites can be performed in different ways. The plastic (or wood flour) can be treated with a diluted solution of vinyl silane/peroxide and the solvent subsequently evaporated before processing. Drawbacks of this method include the use of solvent and that the process is time consuming. Kuan et al. treated wood flour directly with vinyltrimethoxy silane without the use of solvent (28). Another method is to pump the vinyl silane/peroxide solution directly into the extruder during processing. This can be done in a two step process where the first step includes silane grafting of unfilled plastic and the second step incorporation of wood flour. This procedure was used in our first study of silane crosslinked composites (16). In this study, the silane grafting and composite production were carried out simultaneously in a one step process. By doing so, the production of composites is more economical and feasible on an industrial scale, and also gives the possibility of grafting silane onto both polyethylene and wood flour.

This study focused on processing silane crosslinked composites and evaluation of the mechanical properties of the composites. In the processing steps, silane crosslinked composites were produced and thereafter manufactured into rectangular profiles. The composites were cured at different humidities to study how that affects the degree of crosslinking in the composites. Silane crosslinked composites with different degrees of crosslinking were then evaluated regarding their mechanical performance.

Experimental

Materials

High density polyethylene, Exxon Mobile Chemicals HD6733 (MFI=33 g/10min, 190˚C/2.16 kg), was purchased from Channel Prime Alliance (Norwalk, CT, U.S.). Pine wood flour (40 mesh) was provided from American Wood Fiber (Schofield, WI, U.S.). 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, Ohio, U.S.). Throughout this paper the crosslinked composites are in figures and tables referred to as "XLPE40" and the non-crosslinked as "HDPE40". Samples stored at room temperature and in a sauna are abbreviated RT and SA, respectively.

Processing

Compounding

The wood flour was dried for 24 hours 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, Connecticut, USA) co-rotating twin-screw extruder with 7 temperature zones. The plastic (60 % w/w) and the wood flour (40 % w/w) were fed to the extruder at temperature zone 1 with Schenk AccuRate (Whitewater, Wisconsin, USA) gravimetric feeders. *Table 1*, shows the processing parameters during compounding. The zone temperatures ranged between 171-193 ˚C, the screw speed was 200 rpm, the melt pressure at the die varied between 15-39 bar depending on material blend, and the material output was 6.8 kg/h. Silane crosslinked 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 granulated with the use of a Primo 120E (Rieter, Spartanburg, South Carolina, USA) pelletizer.

Profiling

The compounded composite granulates were dried for 24 hours 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 granulates (96 % w/w) and lubricant (4 % w/w) was gravimetrically fed to the extruder at temperature zone 1. As is shown in *Tables 2 and 3*, the processing settings varied depending on material formulation. The temperatures were between 191-116 ˚C, the screw speed between 150-30 rpm, the melt pressure at the die varied between 0-17 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 through the water spray tank. Standard test specimens for mechanical testing were cut from the profiles. Part of the samples was stored at room temperature and the others were stored for 48 hours in a simulated sauna. The storage conditions in the sauna were at 90 ˚C and near saturation. The sauna stored samples were subsequently dried to their initial weight before testing.

Melt flow index, MFI

Melt flow index (MFI) measurements of composite granulates were obtained using a Galaxy I Melt Indexer, Model 750 (Kayeness, Inc., Morgantown, PA, U.S.). The measurements were performed at 190 ºC with a 2.16 kg load in accordance with ASTM D1238 standard.

Gel content

The gel content of the samples was determined using p-xylene extraction according to ASTM D2765. 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 crosslinking 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 hours. Extracted specimens were then dried at 150 ˚C until a constant weight was attained and subsequently re-weighed. The gel content of the different blends was determined as the average of two separate analyses. The gel-content was calculated according to the following equation:

Extract % = (weight lost during extraction) / (weight of original specimen-weight of filler)

Gel content = 100 – Extract % (1)

Mechanical testing

Flexural properties

Flexural properties of the samples were measured on a Tinius Olsen H5K-S UTM equipment (Horsham, PA, U.S.) in accordance with ASTM D790. The dimensions of the specimens tested were approximately 3.2×12.7×130 mm. The measurements were performed at ambient conditions, i.e. a temperature of 23 ˚C and a relative humidity of approximately 50 %. At least ten specimens of each blend were tested.

Impact testing

Instrumented drop weight impact tests were performed on a Dynatup GRC 8250 impact tester (Instron, Norwood, MA, U.S.) at a speed of 1 m/s. The dimensions of the un-notched composite specimens tested were approximately 3.2×12.7×130 mm. The composites were impacted in bending mode, and were not clamped down. A GRC EC 8250 environmental chamber was used to conduct impact tests at -30, 0, 25 and 60 ºC. The specimens to be analysed were kept for at least 30 min at the chosen temperature before performing the test. All the data was analyzed using Instron Dynatup Impulse data acquisition system (Version 2.2.0, Instron, Norwood, MA, U.S.) At least ten specimens of each blend were tested at the four different temperatures.

Creep properties

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 2×12×30 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 ºC.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to monitor the fracture surface of the composites after quenching the composites in liquid nitrogen. SEM analysis was performed using a Hitachi S-4300 field emission SEM (Hitachi Science Systems Ltd, Japan) at an accelerating voltage of 15 kV. The composites were sputtered with a layer of gold/palladium before the measurements.

Results and Discussion

Processing

Compounding

In the compounding step, grafting of vinyltrimethoxy silane onto polyethylene and wood flour and composite production was carried out simultaneously in a one step process. A ratio of approximately 5:1 between residence time in the extruder (at the actual temperatures) and the half life time of the peroxide was used. If the residence time corresponds to five-half lives there will be > 97 % consumption of the peroxide (26). As can be seen in *Table 1*, addition of a solution of vinyltrimethoxy silane (VTMS) and dicumyl peroxide during compounding increased the motor load and melt pressure in the extruder. An increase in melt viscosity of polyethylene upon silane grafting was expected. This increase in melt viscosity is due to premature crosslinking but the melt viscosity will also increase as a result of interaction between grafted silane groups (26). A higher melt viscosity and the volatile compounds created during melt grafting reactions contribute to the increased melt pressure. In our previous study we showed that an addition of 4 % or more of silane solution during the grafting process was necessary to be able to fully crosslink the material at 90 ºC at near saturation within 48 hours (18). The addition of silane solution in this study was limited to 2 % w/w since at higher level of silane solution addition the melt pressure limit of the extruder was reached.

Profiling

The compounded granulates were manufactured into rectangular profiles (6.4 x 60 mm). According to the supplier the melt flow index of the high density polyethylene used was

33. After addition of wood flour to the polyethylene, the melt flow index of the non-crosslinked granulates was still rather high and measured to 4.8. The relatively low melt viscosity of the non-crosslinked composite melt made it difficult to handle downstream through the water spray tank, without creating an irregular structure. As can be seen in *Table 2*, the approach to minimize the irregular structure was to lower the melt temperature by a stepwise decrease in screw speed and heating temperature in the last part of the extruder. A decrease in melt temperature increases the motor load. The use of lubricant and the relatively high heating temperature in the beginning of the extruder made it possible to keep the motor loading down while the melt temperature was decreased. In this way, the surface smoothness and appearance of the non-crosslinked composite profiles was improved. However, it was not possible to achieve a completely smooth surface structure of the non-crosslinked profiles, see *Fig. 3*. The melt viscosity of the crosslinked composites was much higher than for the non-crosslinked composites as a result of premature crosslinking and interaction between grafted silane groups. It was not possible to measure the melt flow index of the crosslinked granulates since the melt viscosity was too high. However, the shear forces introduced during extrusion made it possible to profile the crosslinked composite. The higher melt viscosity of the crosslinked composite made it easier to handle downstream through the water spray tank without creating an irregular structure. As is shown in *Table 3*, the melt temperature was stepwise lowered during profiling of the crosslinked composites until a regular structure was achieved. In our previous study (18), we found that edge-tearing and rough surface of the final crosslinked composites were a problem. In that study no lubricant was used due to the risk of interference with the silane solution during the grafting process. Also in this study, edge-tearing and a rough surface of the crosslinked profiles was a problem when no lubricant was used. These problems are believed to be caused by encapsulating problems of the wood flour. However, the use of 4 % w/w of lubricant removed the rough surface and the edge-

tearing of the crosslinked profiles, see *Fig. 3*. Possible interference between lubricant (modified fatty esters) and silane is not believed to be as critical during the profiling step (second step) as it would be during the grafting step.

Degree of crosslinking

The degree of crosslinking in the composites was determined by gel content measurements. The gel content was determined in accordance with ASTM D2765. Crosslinked polyethylene is insoluble in boiling p-xylene while the non-crosslinked part is soluble. The gel content can thus be determined gravimetrically from the extracted samples. The first step in the crosslinking reaction is hydrolysis of the methoxyl groups to silanol groups. Water is responsible for the hydrolysis of the methoxyl groups. A higher humidity level in the curing process would thus be expected to create a higher degree of crosslinking in the samples. As can be seen in *Table 4*, storage in a high humidity sauna generated a higher degree of crosslinking (59 %) in the composites than storage at room temperature (33 %). In a previous study it was shown that storage of silane modified composites at room temperature did not significantly affect the gel content in the composites (17). The degree of crosslinking in the composites stored at room temperature is thus believed to correspond to the crosslinking that takes place during processing. Earlier studies have shown that the maximum gel content during silane crosslinking is in the range between 75-80 % (17, 27). It was shown that an addition of 4 % w/w or more of the silane solution during processing was necessary to fully crosslink the composites cured at 90 ºC at near saturation, when no catalyst was used. The addition of silane solution in this study was limited to 2 % w/w since at higher level of silane solution addition the melt pressure limit of the extruder was reached. The rate of the crosslinking reaction can be increased by incorporation of a tin based catalyst (dibutyl-tin-dilaurate, DBTDL) during processing (27). Incorporation of such catalyst would increase the rate of crosslinking of the plastic but could on the other hand counteract the reaction with wood. DBTDL has been shown to increase the rate of both the reaction steps in the crosslinking, i.e. hydrolysis and condensation (27). In presence of DBTDL, formation of an ether bond between plastic and wood (-Si-O-Wood) could be catalyst back to a silanol group. The use of catalyst would also make the final composite product more expensive.

Mechanical properties

Flexural properties

The flexural properties of the composites were determined in accordance with ASTM D790. *Fig. 4*, shows characteristic stress-strain curves of the composites. The crosslinked composites showed flexural strength superior to the composites to which no silane was added. In our previous study, silane crosslinked composites also showed flexural strength superior to the non-crosslinked composites (18). In that study, the flexural strength was shown to pass through a maximum between 2-3 % w/w of added silane solution and then decreased slowly. Improved adhesion between the wood and the polyethylene matrix is most likely the reason for the significant improvement in flexural strength of the crosslinked composites. The improved adhesion could be due to covalent bonding between wood and 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, see *Fig. 5*. Curing the crosslinked composites in a high humidity sauna increased the degree of crosslinking in the composites significantly (i.e. 33 to 59 %). Even so, the flexural strength of the composites cured in a sauna did not differ much from the crosslinked 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 temperature used during processing. All the mechanical data from the flexural testing are summarised in *Table 5*. The elongation at break was also higher in the crosslinked composites than for the non-crosslinked. Improved adhesion between wood and polyethylene in the crosslinked composites is believed to explain the improved toughness. Without interfacial adhesion, the gap between the wood and polyethylene phases provides an area of weakness, which easily propagates a crack through the material.

There was no significant difference in flexural modulus between the crosslinked and non-crosslinked composites. However, the crosslinked composites seem to have a slightly higher flexural modulus than the non-crosslinked composites. In our previous study, the flexural modulus of silane crosslinked composites was shown to be lower than for the non-crosslinked, and was also shown to decrease at increased level of added silane solution. The decrease in flexural modulus was shown to correlate well with the crystallinity of the polyethylene matrix in the composites. At higher level of silane addition the premature crosslinking during processing increased and thereby lowered the degree of crystallinity as a result of restriction in macromolecular flexibility in the melt. In this study, the addition of silane solution was rather low (2 % w/w) and the premature crosslinking that took place during processing was also shown to be low (33 %). The rather low degree of premature crosslinking during processing is believed to explain why no decrease in flexural modulus was observed. The increased crosslinking that occurs during curing in a sauna occurs when the composite is in the solid state. Therefore, the crystalline phase of the HDPE should not undergo considerable changes and the crosslinking preliminary should take place only in the amorphous phase. This explains why there is no significant change in flexural modulus between the crosslinked composites stored in a sauna and at room temperature.

Impact Strength

Instrumented drop weight impact tests on un-notched composite specimens were carried out. The test was performed to study the effect of temperature on the impact properties of crosslinked and non-crosslinked composites. *Fig. 6*, illustrates characteristic force-deflection curves from impact testing of the composites stored at room temperature. As can be seen in the figure, the crosslinked and the non-crosslinked composites shows relatively linear loading curves, ending in a rather sharp drop after reaching maximum load. The maximum load and deflection at failure was significantly higher for the crosslinked than for the non-crosslinked composites. This reveals a higher impact resistance in the crosslinked composites than in the non-crosslinked. The effect of temperature on the impact strength of the composites is presented in *Fig. 7* and *Table 6*. Independent of temperature, the impact strength was significantly higher (about two times) in the crosslinked composites than in the non-crosslinked. Improved adhesion between wood and polyethylene and improved impact strength of the polyethylene matrix upon crosslinking, can explain the superior impact strength of the crosslinked composites. In the temperature range -30 to 60 ºC, it is difficult to make certain statements about trends in impact strength among the crosslinked and non-crosslinked composites since the standard deviation within the two groups is overlapping. The trend, however, seem to be a slightly higher impact strength at -30 ºC than at 0º and at 25 ºC, and then an increase in impact strength at 60 ºC. High density polyethylene has two major transitions when heat treated, corresponding to γ-transition occurring at about -128 ˚C and then the α-transition at about 113 ˚C (29). Unplasticized HDPE does not display an apparent β-transition because its crystallinity greatly reduces the relaxation intensity (29). The impact strength of the composites was thus determined in a temperature range in between the two major temperature transitions of high density polyethylene. This might explain why the impact strength did not differ significantly in the temperature range -30 to 60 ˚C within the two composite blends. It is interesting to note that the increase in impact strength at 60 º was more significant for the crosslinked composite than for the non-crosslinked. Crosslinked polyethylene was introduced on the market to improve the temperature durability of polyethylene (27). One could thus expect the crosslinked composite to perform better at higher temperature than the non-crosslinked composite.

Short-term creep

Short-term creep experiments were performed using a dynamic mechanical thermal analyzer, DMTA V. The experiments were performed to study the effect of silane crosslinking on the creep properties of the composites. In *Fig. 8*, the results from the short-term creep test of non-crosslinked and crosslinked (stored in a sauna) composites are shown. The creep response after 3 days of loading was significantly lower in the crosslinked composites than in the non-crosslinked composite. It is interesting to note that the creep rate (mm/day) during loading is more than twice as fast for the non-crosslinked composite than for the crosslinked. After 3 days of recovery the non-recoverable deformation was also larger in the non-crosslinked composite (0.66 %) than in the crosslinked (0.23 %). The improved creep properties of the crosslinked composites are believed to be related to a reduced viscous flow of the polyethylene matrix due to crosslinking as well as improved adhesion between the polyethylene matrix and wood flour. In an earlier study of silane crosslinked composites, it was also shown that a higher degree of crosslinking lowered the creep response (17). In that study, crosslinked composites stored in a sauna showed lower creep response than composites stored at room temperature.

Scanning electron microsscopy (SEM)

Scanning electron microscopy (SEM) was used to monitor the fracture surface of the composites after quenching the samples in liquid nitrogen. In *Figs. 9 and 10*, respectively, the fracture surfaces of non-crosslinked and crosslinked composites are shown. A comparison of the overview micrographs of the non-crosslinked (*Fig. 9a and d*) and the crosslinked (*Fig 10a and d*) composite shows that it is much easier to visualise the wood filler in the non-crosslinked composite than in the crosslinked where the wood filler to a greater extent is covered with matrix. The fracture surface of the non-crosslinked composite shows several holes and patterns from wood fibres which were so weakly bonded to the matrix that they were released from the matrix during fracture. In the upper right corner and on the left side of micrograph *9a)* examples of such holes and patterns from released wood fibres are shown. In the magnified micrographs *9c)* and *f)* it is also possible to notice distinct gaps between the matrix and the wood fibres, indicating poor adhesion. In the crosslinked composite (sauna stored), on the other hand, there is no gap between the matrix and the wood fibre, indicating good interfacial adhesion. This is visualised in the magnified micrographs *10c)* and *f)*. In micrograph *10f)* it is also possible to picture wood fibres covered with a thin layer of polyethylene matrix. In addition, the crosslinked composites show almost no signs of fibre pull-outs and most of the fibres fractured.

Conclusions

Silane crosslinked composites were produced during compounding in a co-rotating twin-screw extruder. Addition of silane solution during compounding increased the melt viscosity significantly as a result of both premature crosslinking and interaction between grafted silane groups. Composite granulates were subsequently extruded into rectangular profiles. The higher melt viscosity of the crosslinked composite than the non-crosslinked made it easier to handle downstream without creating an irregular structure. On the other hand, edge-tearing and a rougher surface on the crosslinked composites were a problem during profiling. Addition of lubricant removed the rough surface and the edge-tearing on the crosslinked profiles. The crosslinking reaction was shown to be initiated already during the processing steps. Storage in a high humidity sauna at 90 ˚C generated a higher degree of crosslinking in the composites than storage at room temperature.

The flexural strength and elongation at break was significantly higher in the silane crosslinked composites than in the non-crosslinked. The improved toughness in the crosslinked composites is most likely caused by improved adhesion between the wood and polyethylene phases. There was no significant difference in flexural modulus between the crosslinked and non-crosslinked composites, although the crosslinked composites seem to have a slightly higher modulus. Impact testing showed that the impact strength of the crosslinked composites was considerable higher (at least double) than the non-crosslinked. This was explained as a result of both improved adhesion between wood and polyethylene and improved impact strength of the polyethylene matrix upon crosslinking. In the temperature range -30 to 60 ºC, the trend in impact strength among the crosslinked and non-crosslinked composites indicated slightly higher impact strength at -30 ºC than at 0º and at 25 ºC, and then an increase in impact strength at 60 ºC. The increase in impact strength at 60 ºC was also more significant for the crosslinked composites than for the non-crosslinked. Moreover, short-term creep analysis showed that the creep response during loading in the crosslinked composites was significantly lower than in the non-crosslinked. After recovery the unrecoverable part was also larger in the non-crosslinked composite than in the crosslinked. The improved creep properties of the crosslinked composites was related to a reduced viscous flow due to crosslinking, as well as to improved adhesion between the polyethylene matrix and wood flour.

Scanning electron microscopy analysis on the fracture surface of the non-crosslinked composite showed holes in the matrix from pulled out fibres. In addition there were distinct gaps between the polyethylene and the wood, indicating poor interfacial adhesion. The crosslinked composites, on the other hand, showed no gap between the polyethylene and the wood, indicating good interfacial adhesion. Moreover, the crosslinked composites showed almost no signs of fibre pull-outs and most of the fibres fractured.

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Legend to figures

Fig. 1. The reaction mechanism during a) peroxide induced melt grafting of vinyltrimethoxy silane onto polyethylene, b) radical induced crosslinking of polyethylene

Fig. 2. The hydrolysis step (1) and condensation step (2) during silane crosslinking.

Fig 3. a) The final appearance of the crosslinked and non-crosslinked siding profiles.
b) Magnification of the profiles in figure a).

Fig.4. Characteristic stress-strain curves of the composites.

Fig 5. Proposed bonding mechanisms in the silane crosslinked composites. Covalent bonding between wood and polyethylene through condensation 1) and free radical reaction 2). Secondary interactions through hydrogen bonding 3) and van der Waals interaction 4).

Fig 6. Characteristic force-deflection curves from impact testing of the composites stored at room temperature.

Fig 7. The effect of temperature on the impact strength of the composites.

Fig 8. Strain as a function of time during creep experiments at 30 ºC. A constant stress of 3 MPa was applied during the loading time.

Fig. 9. Scanning electron microscopy analysis of the fracture surface of the non-crosslinked composite at a) ×120 b) ×600 c) ×2000 d) ×120 e) ×600 f) ×3000

Fig. 10. Scanning electron microscopy analysis of the fracture surface of the crosslinked composite at a) ×150 b) ×800 c) ×3500 d) ×100 e) ×800 f) ×2500

Figure 1. Bengtsson, Stark, and Oksman

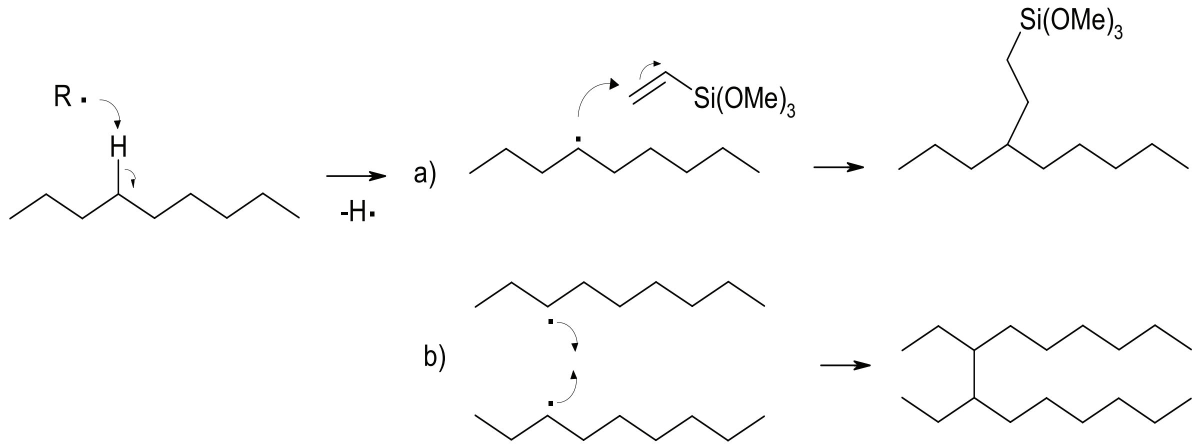
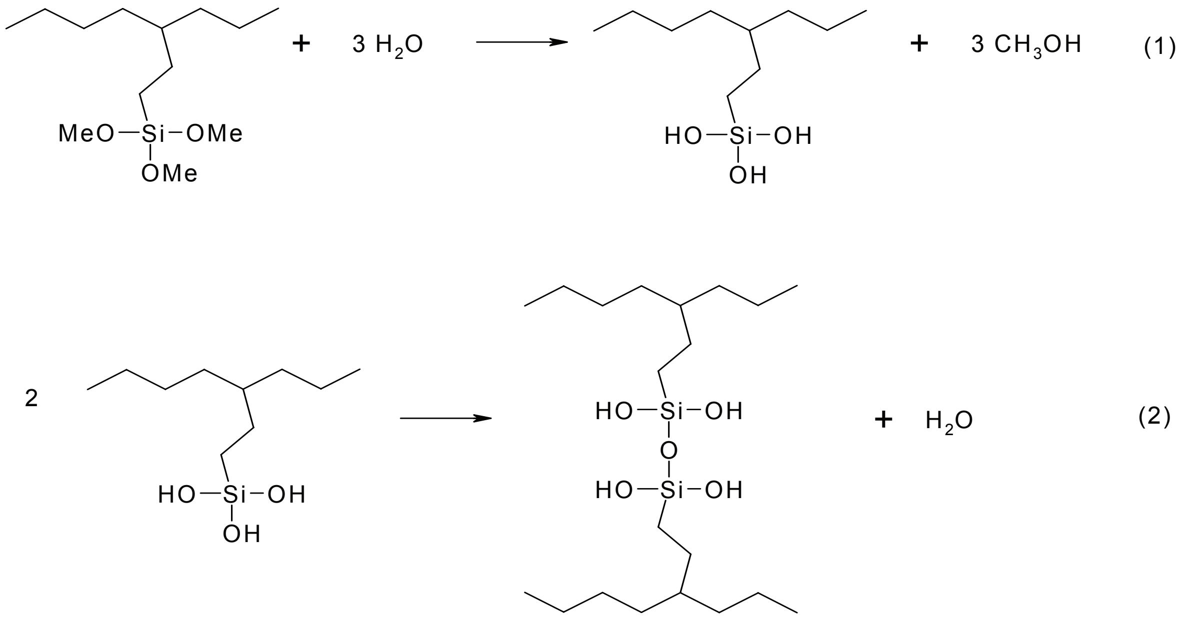


Figure 2. Bengtsson, Stark, and Oksman



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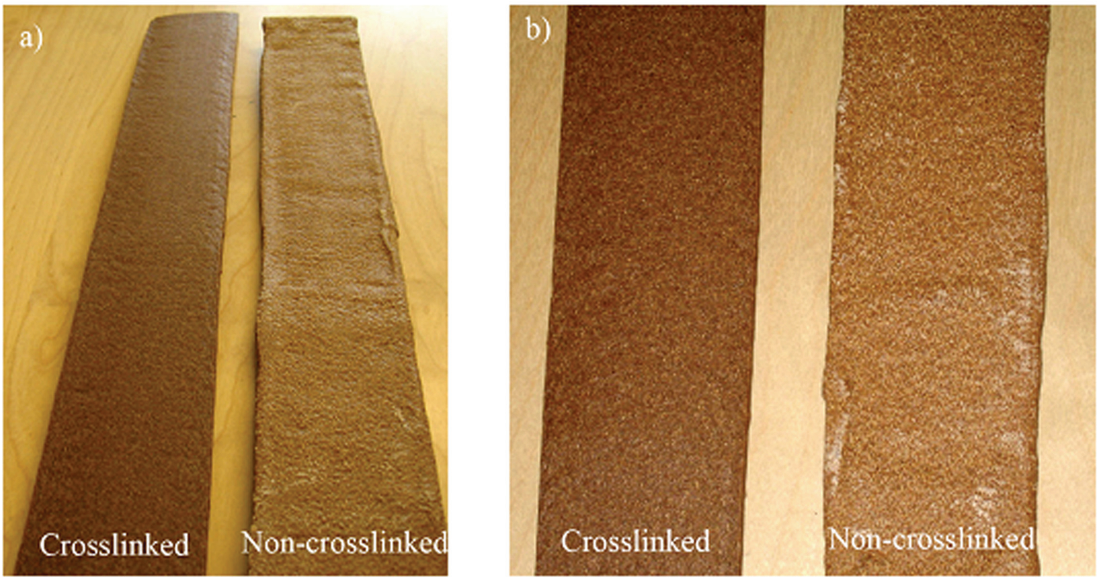

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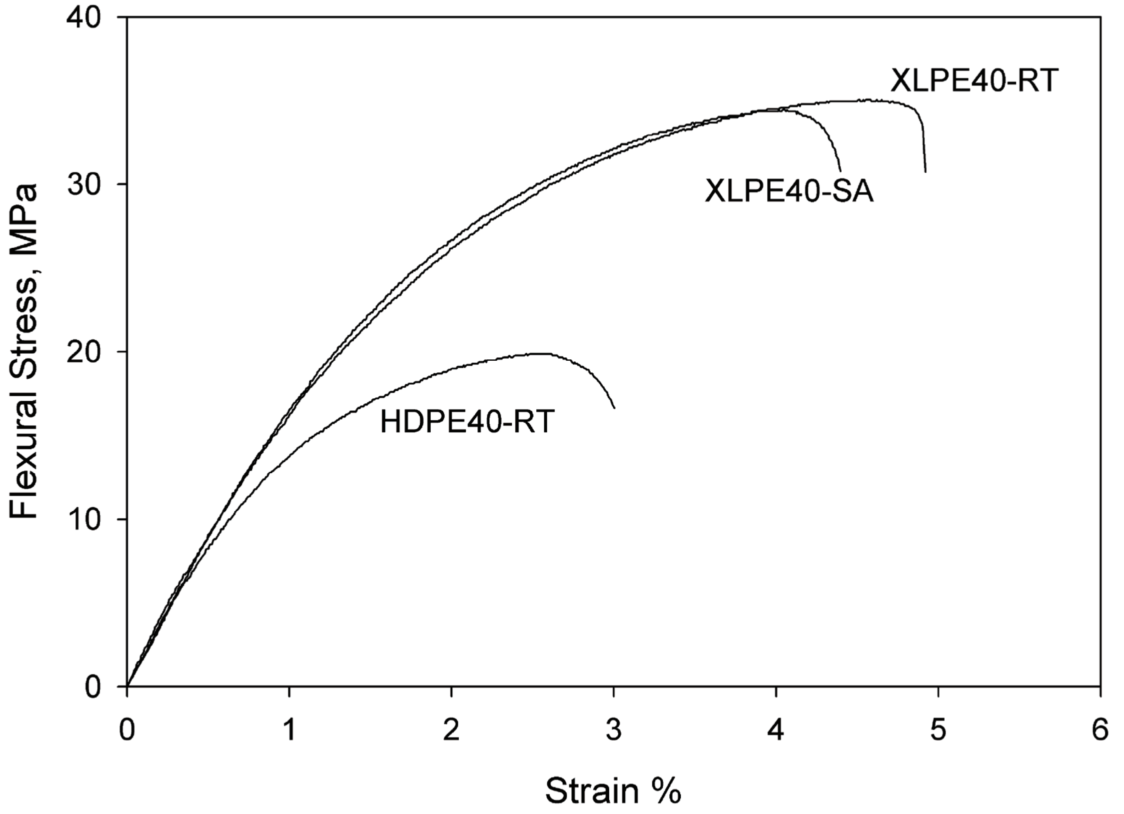

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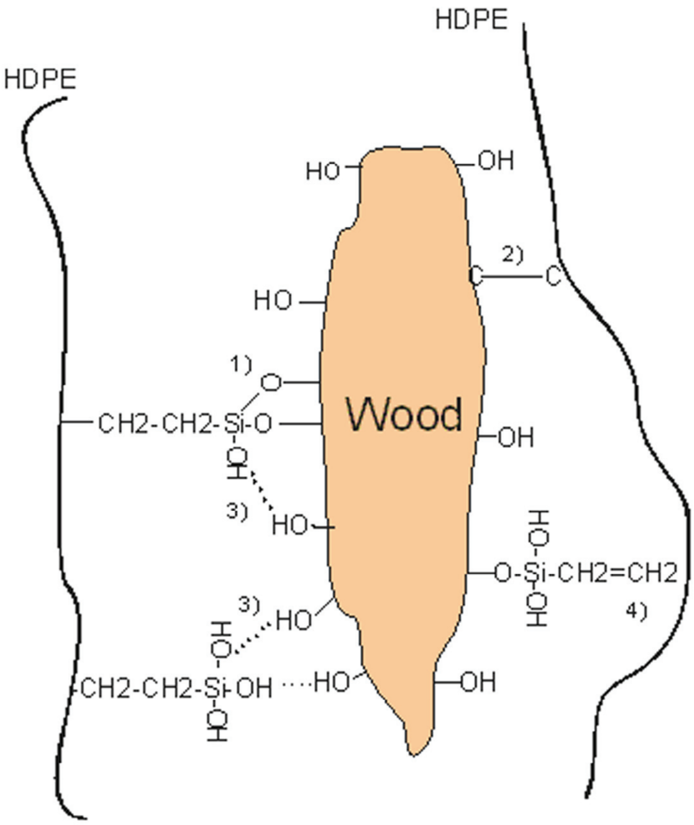

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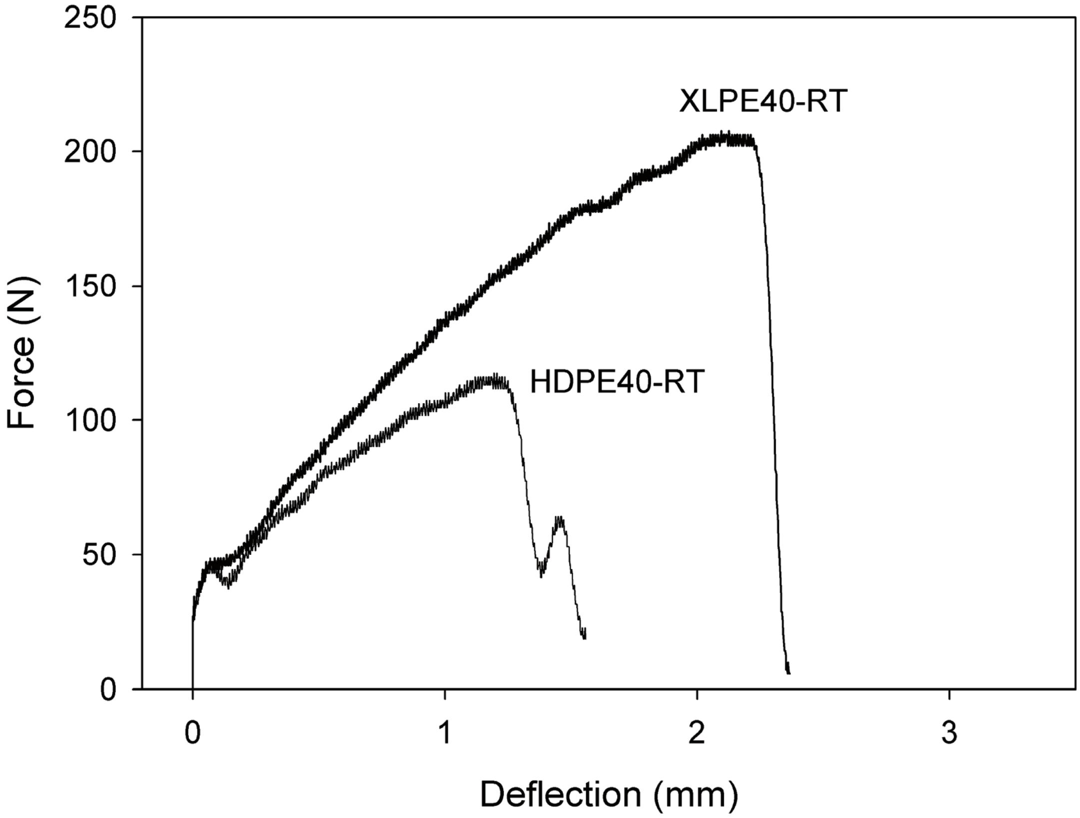

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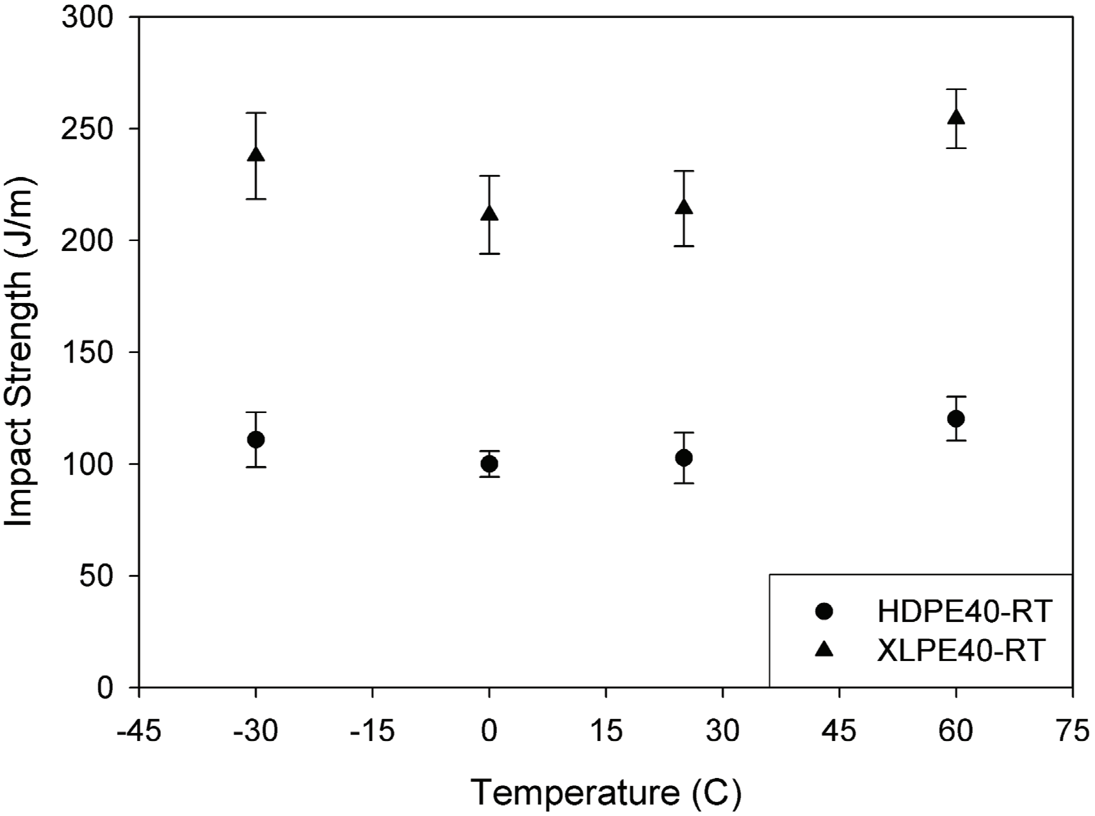


Figure 8. Bengtsson, Stark, and Oksman

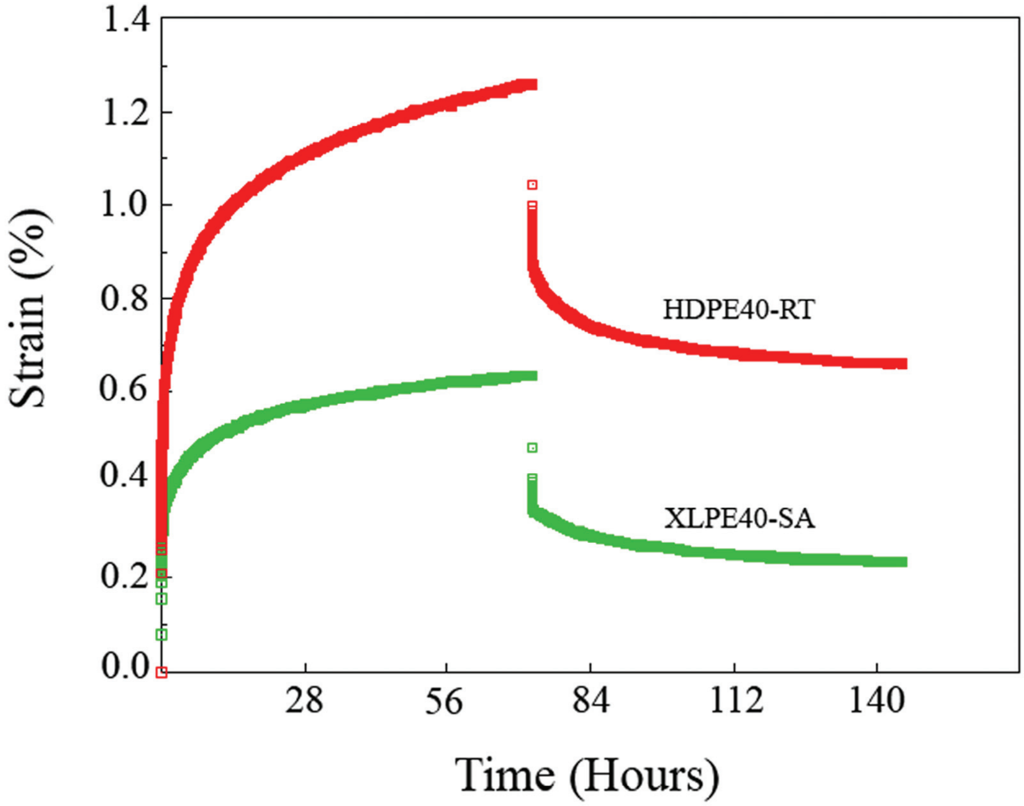
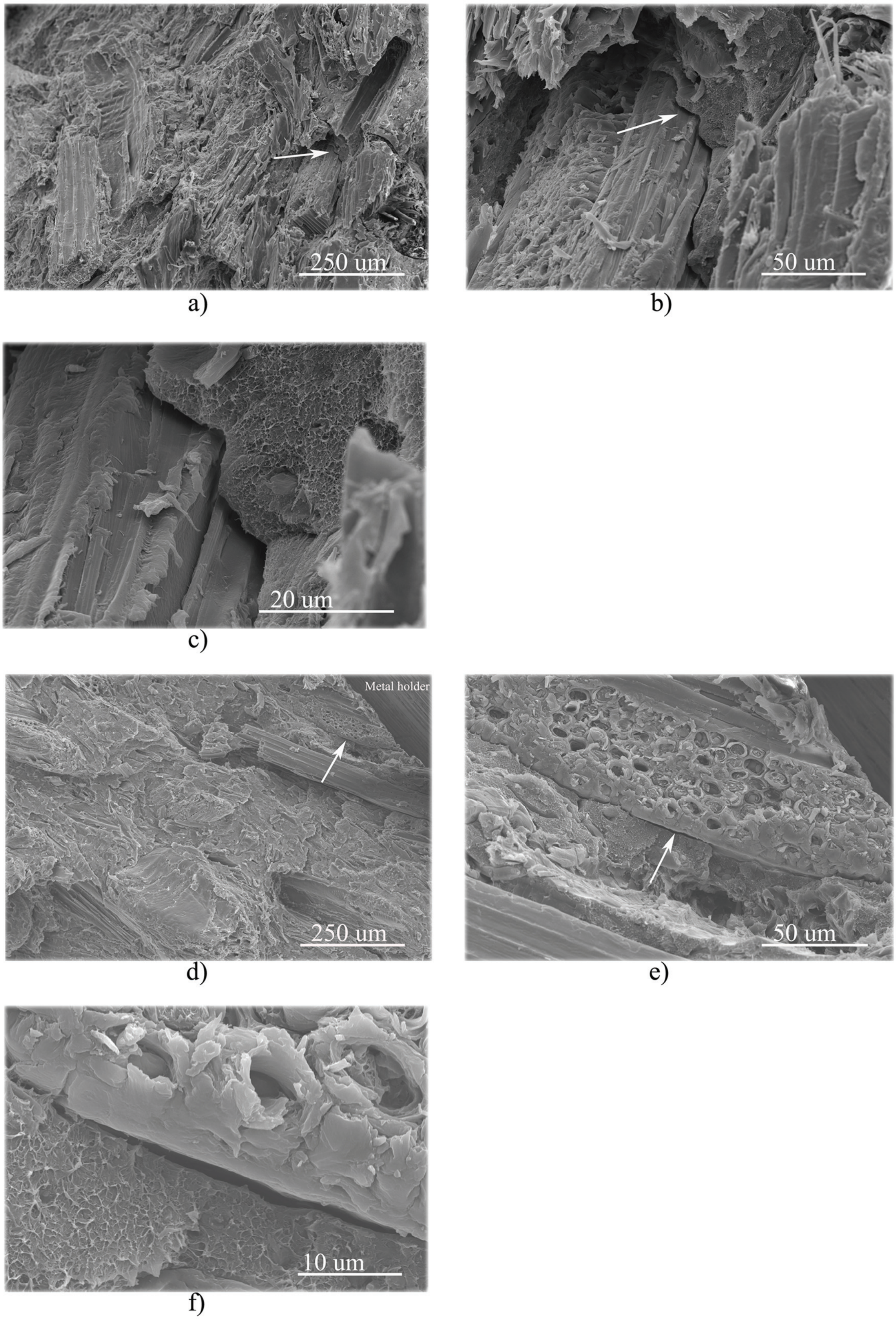


Figure 9. Bengtsson, Stark, and Oksman



a)

b)

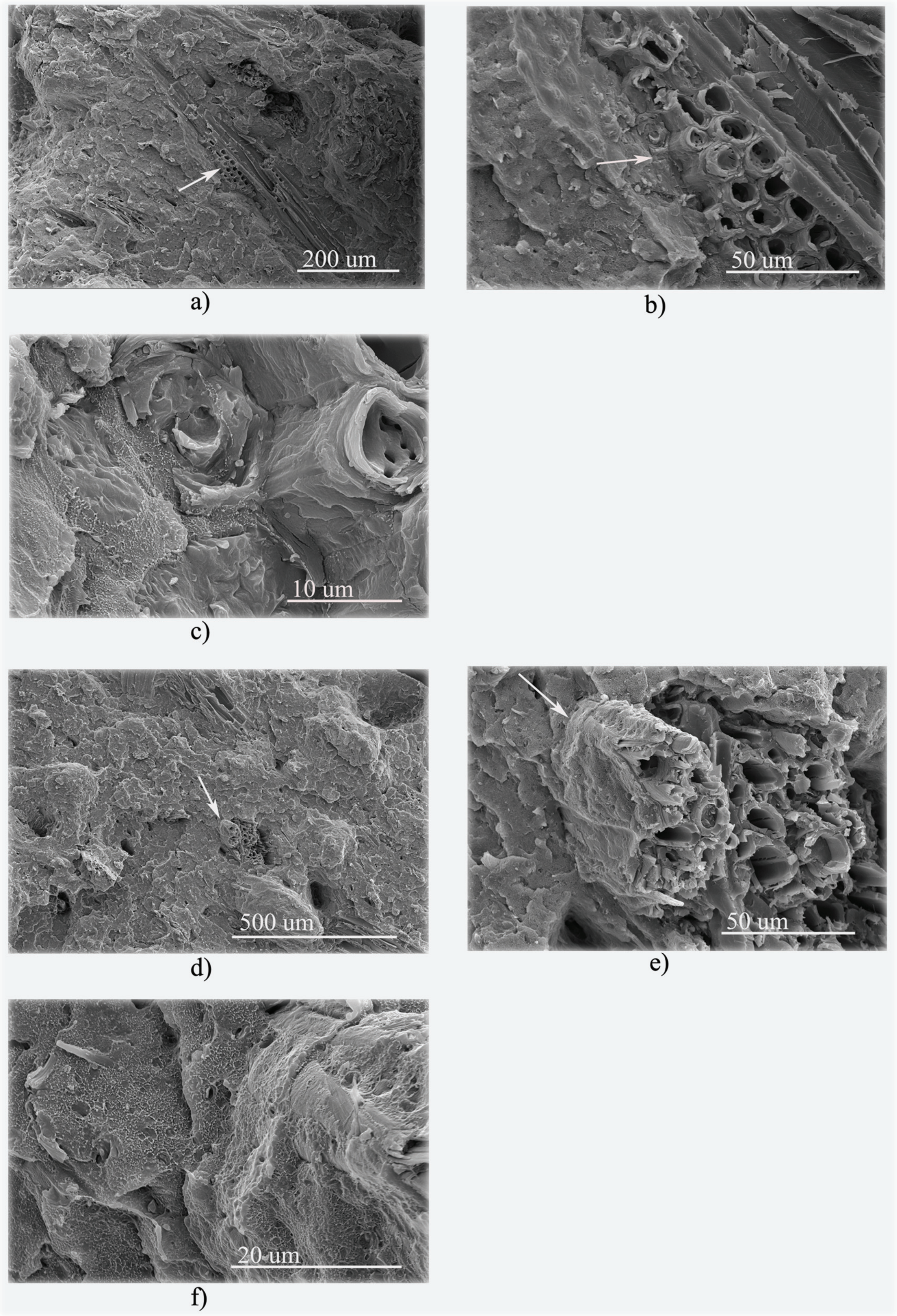
c)

d)

e)

f)

Figure 10. Bengtsson, Stark, and Oksman



a) b) c) d) e) f)

Table 1. Processing settings during compounding

	Non-crosslinked (HDPE40)	Crosslinked (XLPE40)
Overall rate (kg/h)	6.82	6.82
Plastic feeder (kg/h)	4.09	3.95
Wood feeder (kg/h)	2.73	2.73
Silane solution (kg/h)[1]	-	0.14
Feed section (º C)	20	20
Zone 1 (º C)	193	193
Zone 2 (º C)	188	188
Zone 3 (º C)	174	174
Zone 4 (º C)	174	174
Zone 5 (º C)	174	174
Zone 6 (º C)	171	171
Zone 7 (º C)	171	171
Die	174	174
Vent pressure Zone 8	Vaccum	Vaccum
Screw speed (rpm)	200	200
Melt temperature (º C)	186	188
% Load	29	43
Melt pressure (bar)	15	39

[1] A solution of vinyltrimethoxy silane and dicumylperoxide (12:1)

Table 2. Processing setting during profiling of non-crosslinked composites (HDPE40)

Formulation	**1**	**2**	**3**	**4**	**5[1)]**
Overall rate (kg/h)	6.82	6.82	6.82	6.82	6.82
Composite feeder (kg/h)	6.82	6.82	6.82	6.55	6.55
Lubricant feeder (kg/h)	-	-	-	0.27	0.27
Feed section (º C)	20	20	20	20	20
Zone 1 (º C)	188	166	166	182	182
Zone 2 (º C)	188	160	160	182	182
Zone 3 (º C)	188	160	160	177	177
Zone 4 (º C)	188	154	154	143	143
Zone 5 (º C)	188	149	149	127	127
Zone 6 (º C)	188	149	149	121	118
Zone 7 (º C)	182	149	149	121	116
Die	177	143	143	132	132
Die 2	160	143	143	135	135
Vent pressure Zone 8	Vaccum	Vaccum	Vaccum	Vaccum	Vaccum
Screw speed (rpm)	150	150	40	30	30
Melt temperature (º C)	183	150	145	129	129
% Load	28	31	85	50	48
Melt pressure (bar)	0	0	0	6	14

[1)] The composite formulation used for testing

Table 3. Processing setting during profiling of crosslinked composites (XLPE40)

Formulation	**1**	**2**	**3**	**4**[1)]
Overall rate (kg/h)	6.82	6.82	6.82	6.82
Composite feeder (kg/h)	6.55	6.55	6.55	6.55
Lubricant feeder (kg/h)	0.27	0.27	0.27	0.27
Feed section (º C)	20	20	20	20
Zone 1 (º C)	188	188	188	188
Zone 2 (º C)	188	188	188	188
Zone 3 (º C)	188	188	177	177
Zone 4 (º C)	188	188	166	154
Zone 5 (º C)	188	188	154	149
Zone 6 (º C)	177	177	149	143
Zone 7 (º C)	177	177	149	143
Die	182	182	177	177
Die 2	191	191	179	179
Vent pressure Zone 8	Vacuum	Vacuum	Vacuum	Vacuum
Screw speed (rpm)	100	50	50	30
Melt temperature (º C)	184	183	171	168
% Load	27	30	34	47
Melt pressure (bar)	16	17	12	13

[1)] The composite formulation used for testing

Table 4. Gel content of the composites

Sample code	Gel content (%)
HDPE40-RT	0
XLPE40-RT	33
XLPE40-SA	59

Table 5. Flexural properties of the composites

Sample code	Modulus (GPa)	Strength (MPa)	Strain at max (%)
HDPE40-RT	1.6 ± 0.2	19.4 ± 2.3	2.8 ± 0.7
XLPE40-RT	1.9 ± 0.3	36.2 ± 3.0	4.5 ± 0.2
XLPE40-SA	1.9 ± 0.2	33.9 ± 2.2	3.9 ± 0.2

Table 6. Impact strength (J/m) of the composites at different temperatures

	Temperature (º C)			
Sample code	**-30**	**0**	**25**	**60**
HDPE40-RT	111 ± 12	100 ± 12	102 ± 11	120 ± 10
XLPE40-RT	238 ± 19	211 ± 26	214 ± 17	254 ± 13