

Jie Duanmu<sup>a</sup>  
E. Kristofer Gamstedt<sup>b</sup>  
Ari Rosling<sup>a</sup>

<sup>a</sup> Laboratory of Polymer  
Technology,  
Åbo Akademi University,  
Biskopsgatan 8,  
FIN-20500 Åbo, Finland

<sup>b</sup> KTH Fibre and Polymer  
Technology,  
Royal Institute of Technology,  
Stockholm, Sweden

## Synthesis and Preparation of Crosslinked Allylglycidyl Ether-Modified Starch-Wood Fibre Composites

Native potato starch has been modified with allylglycidyl ether (AGE) under various reaction conditions including different sodium hydroxide and AGE concentrations, reaction temperatures and times. <sup>1</sup>H-NMR and FT-IR were used to analyze the products. AGE-modified starch, with two degrees of substitution (DS), namely DS = 1.3 and DS = 2.3, was synthesized and used for preparation of a new family of crosslinked composites reinforced with various amounts of bleached softwood fibres. Composite premixes of modified starch, wood fibres and ethylene glycol dimethacrylate (EGDA) were cured in a hot press using 2% (w/w) of benzoyl peroxide at 150°C under high pressure for 10 min. The matrix with high degree of substitution exhibited good processability and was easily processed even for the highest fibre contents, up to 70% (w/w). In addition, scanning electron micrographs showed good dispersion and adhesion between the starch matrix with high degree of substitution and fibre. The original poor mechanical properties of the cured modified starch were markedly improved by the addition of wood fibres. In the extractions tests cured high-DS and low-DS composite samples showed weight losses in the range of 1 and 15% (w/w), respectively. No unreacted crosslinker ethylene glycol dimethacrylate was detected in the solutes as determined by NMR.

**Keywords:** Native potato starch; Modified starch; Crosslinked starch; Modulated differential scanning calorimetry; Wood fibre; Composite

### 1 Introduction

Starch is one of the most abundant polymers in nature. It is cheap, renewable, biodegradable and has found its use as a substitute for traditional petroleum-based polymers in many industrial products, such as compostable plastics for packing applications and household items [1]. Natural starch can be rendered suitable for traditional melt processing by addition of plasticizing additives [2–4]. Alternatively, hydrophobization reactions by chemical derivatization to alkyl ethers [5a–d] and esters [6a–c], polymer grafting [7, 8] and multiphase blends [9, 10] are well known and improve the thermoplasticity and water resistance of starch. The literature on preparation of alkyl-etherified starch by terminal epoxy compounds is very sparse [5c, 11a–d]. Unfortunately, the hydrophilicity and poor mechanical properties often still remain limiting factors for the use of thermoplastic starch in many applications. Preparation of crosslinked starch has been studied

by several groups [12, 13]. The material properties have ranged from highly hydrophilic viscous hydrogels to extremely brittle solids depending on applied reagents and reaction conditions. Biofibres have been tested for their reinforcing effect in traditional petroleum-based polymers [9, 10, 14] and in native polymers [15, 16]. Despite many positive attributes, cellulose fibres are connected with two major drawbacks, hygroinstability [17] and incompatibility especially with traditional hydrophobic plastics [14]. The similarity in chemical structure between a starch matrix and cellulose fibres is expected to increase the compatibility and improve the overall performance of the starch composite [18].

The present work was undertaken to prepare and evaluate an environmentally-friendly material composed of wood fibres in a thermoset starch matrix. We have studied the effect of various reaction parameters on the modification of starch with allylglycidyl ether under aqueous alkaline conditions and estimated the degree of substitution with proton nuclear magnetic resonance, <sup>1</sup>H-NMR. The modification of starch by allylglycidyl ether (AGE) should serve several purposes; it provides the starch matrix with unsaturated carbon-carbon double

**Correspondence:** Ari Rosling, Laboratory of Polymer Technology, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo, Finland. Phone: +358-2-2154236, Fax: +358-2-2154866, e-mail: ari.rosling@abo.fi.

bonds to produce the desired crosslinked matrix which limits excessive macromolecular motion, and secondly, it reduces the hydrophilicity of starch and limits its water uptake and swelling. Premixes of AGE-modified starch, various amounts of wood fibres and ethylene glycol dimethacrylate as crosslinker have been prepared and cured under high pressure and temperature with benzoyl peroxide. The composites were studied by scanning electron microscopy (SEM) for their microstructure and spatial fibre distribution, and by solvent extraction to test their gel content. The resulting hygro-mechanical properties are presented in a separate paper [19]. These tests show that the composites with high degree of substitution possess improved hygrostability, stiffness and strength.

## 2 Materials and Methods

### 2.1 Materials

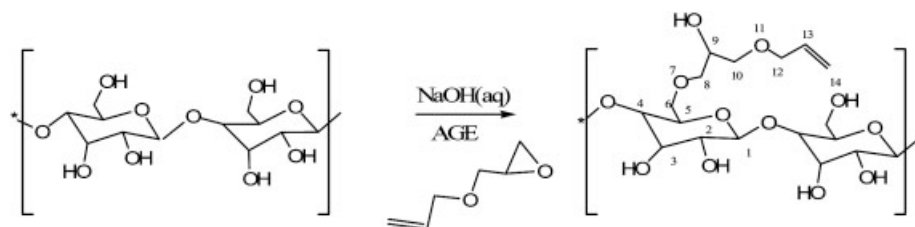
Native potato starch was received as a gift from Lyckeby Stärkelsen, Kristianstad, Sweden. Bleached kraft softwood pulp fibres were supplied by Imatra Mills of Stora Enso (Imatra, Finland). Allylglycidyl ether (AGE, 99%, w/w) was purchased from Aldrich (St. Louis, MO, USA). Benzoyl peroxide (BPO, 70%, w/w) and ethylene glycol dimethacrylate (EGDA, 97%, w/w) were obtained from Fluka Chemika, Buchs, Switzerland). Chloroform-*d* (99.8 atom % D) and deuterium oxide (99.8 atom % D) for NMR analysis were purchased from Acros (New Jersey, USA). All chemicals were used as received.

### 2.2 General procedure for synthesis of AGE modified starch (Scheme 1)

An aqueous starch solution (25%, w/w) was prepared by adding 1 g of starch and 4 g of water into a 100-mL three-necked flask and heated to a predetermined temperature (varied from 65–95°C, cf. Tab. 1) in an oil bath under stirring. To the warm viscous starch solution, a 40% (w/w) aqueous sodium hydroxide solution was added, which varied from 1–2 mol NaOH per anhydro-D-glucose (AGU) unit of the starch (Tab. 1). After 1 h, a predetermined amount of AGE was added to the reaction solution (see Tab. 2). The reaction solution was heated for 16–24 h (see Tab. 2) after which the major part of the water was evaporated from the reaction mixture leaving a high viscous gel. The residual gel was cooled to ambient temperature and the modified starch was precipitated from acetone. The liquid was decanted and the modified starch was further washed four times with acetone. The purified modified starch was dried (for analysis purposes) or mixed with a certain amount of water or ethanol to form a homogeneous solution for further use.

### 2.3 Composite preparation and curing

The example is given for the preparation of the composite LDS-40 made of allyl glycidyl ether-modified starch with a low degree of substitution (DS = 1.3, i.e. LDS) with 40% (w/w) wood fibre. An amount of 1.2 g LDS was added gradually into a glassware containing 45 mL water (ethanol if corresponding highly substituted starch, HDS was



**Scheme 1.** Modification of potato starch with allylglycidyl ether.

**Tab. 1.** Different amounts of NaOH and reaction temperatures used in the LDS starch modification reaction.

Starch (AGU) [mmol]	NaOH [mmol]	AGE [mmol]	Ratio	Temperature [°C]	Time [h]	DS
6	9	18	1:1.5:3	65	24	1.5
6	9	18	1:1.5:3	85	24	1.3
6	9	18	1:1.5:3	95	24	1.2
6	6	18	1:1:3	85	24	1.2
6	9	18	1:1.5:3	85	24	1.3
6	12	18	1:2:3	85	24	0.9

**Tab. 2.** Effect of reaction times and AGE concentrations in the LDS and HDS starch modification reaction.

Starch (AGU) [mmol]	NaOH [mmol]	AGE [mmol]	Ratio	Temperature [°C]	Time [h]	DS
12	18	36	1: 1.5: 3	85	16	1.1
					20	1
					24	1.3
12	18	84	1: 1.5: 7	85	18	1.9
					20	2.2
					24	2.3
6	9	54	1: 1.5: 9	85	14	3

used) during continuous mechanical stirring, after which 5.1 g of wet fibres (21.6%, w/w, fibres in water) was added to the glass vessel. The slurry was heated to 70°C in a water bath and air was blown into the vessel to improve solvent evaporation while stirring at a speed of 300 rpm. When 30 g of water had evaporated (roughly 60%), as measured gravimetrically, the glassware was cooled to 45°C. A 10 mL ethanolic solution of EGDA (0.456 g, 2.3 mmol) and BPO (0.024 g, 0.0001 mmol, 2%, w/w) was added to the mixture. The stirring was stopped after another 15 min and the evaporation of volatiles was continued by applying vacuum by water suction. Evaporation was stopped when constant weight was reached (approximately 2 h for LDS and 1.5 h for HDS composites). The dried mixture of 0.4 g was placed into a steel mould, which was placed between the two heating plates of a pressing apparatus preheated to 150°C. The composite sample was cured by applying a 150 bar pressure (according to the used Carver press machine) for 10 min.

The fibre content is indicated by the weight percentage. The LDS-60, HDS-40 and HDS-60 samples were made similarly. HDS-0 was prepared without fibre at 30 bar. The HDS-70 sample was cured under 200 bar due to its higher viscosity.

## 2.4 Methods

### 2.4.1 NMR and DS

The starch was dissolved in deuterium oxide or DMSO- $d_6$  (10%, w/w), and  $^1\text{H}$ -NMR spectra were collected with a Bruker 250 and 600 MHz spectrometer. Proton spectra were referenced internally to the solvent signal of  $\text{D}_2\text{O}$  or  $\text{CDCl}_3$ , at 4.64 ppm and 7.26 ppm, respectively. The following equation was used for a rough estimation of the AGE substitution degree by  $^1\text{H}$ -NMR

$$\text{DS} = \frac{6 \text{ S1}}{\text{S3} - 7 \text{ S1}} \quad (1)$$

where S1 is the AGE methine proton integral at 5.8 ppm and S3 is the multiplet signal integral at 3.0 – 4.3 ppm comprised of six protons from the AGU and seven protons from the AGE unit.

### 2.4.2 FT-IR

The modified starch with lower and higher DS and the cured composite samples were pulverized and analyzed by a Perkin-Elmer FT-IR spectrometer (Norwalk, CT, USA) equipped with an attenuated total reflection infrared (ATR) mode, using the DuraScopeTM from SensIR Technologies (Wiesbaden, Germany).

### 2.4.3 SEM analysis

The samples were viewed with LEO 1530 SEM (Oberkochen, Germany) working at 15 kV. Composite samples were cut and the cross-sections were polished with 2400 grit silicon carbide paper and sputtered with carbon.

### 2.4.4 Modulated temperature differential scanning calorimetry (MDSC)

The thermal behaviour of native potato starch (NS), LDS and HDS was investigated by means of modulated differential scanning calorimetry (MDSC). All samples were dried in a vacuum oven (133 Pa) for 24 h at 50°C before the analysis. MDSC experiments were carried out using a TA Q1000 instrument (New Castle, NJ, USA) equipped with an auto sampler and a refrigerated cooling system. Aluminium hermetical pans were used and the sample weight varied between 4–5 mg. The scan intervals ranged from –90 to 240°C, a heating rate of 5°C/min was chosen and the modulation was set at  $\pm 1^\circ\text{C}$  for every 60 s. These conditions were selected to minimize error that may result from incomplete modulation of the sample volume [20]. The purge gas was nitrogen.

### 2.4.5 Extraction of composites

Extractions with boiling solvents in a Soxhlet apparatus were performed to evaluate the gel content and the possible extractable reagents in the cured samples. The LDS and HDS samples were extracted by refluxing in a water/ethanol mixture (1:1) and chloroform, respectively, for 24 h.

## 3 Results and Discussion

The literature presents several studies of starch modification performed in organic solvents [21] or biphasic media with water [22]. Realizing the hazards of organic solvents in industry, allylglycidyl starch ethers of low and high DS (roughly 1.3 and 2.3, respectively) were synthesized by reacting AGE with native potato starch under various alkaline conditions and moderate temperatures to obtain optimal reaction parameters in aqueous media. The DS value is defined as how many of the hydroxyl groups on the AGU units are substituted, i.e.  $DS = 3$  corresponds to substitution of all three hydroxyl groups on the AGU units. However, when allyl glycidyl ether reacts with starch, a new hydroxyl group is formed, which is available for further incorporation of allyl glycidyl ether moieties, thus the theoretical DS can exceed a value of 3 [11a]. Consequently, the use of molar substitution (MS) would in this case be more correct to describe the extent of AGE substitution.

### 3.1 Synthesis of AGE-modified starch

Aqueous starch solutions, even with small dry weights, are highly viscous due to the gelatinization phenomenon of starch. The viscosity can be reduced by increasing the solution temperature or by alkaline treatment, e.g. with sodium hydroxide, which disrupt the strongly hydrogen bonded structure between the polymer chains in starch. To study the effect of the reaction temperature on the AGE modification of starch, an aqueous potato starch (20%, w/w) slurry was heated to various temperatures (Tab. 1), followed by the addition of an aqueous sodium hydroxide solution (40%, w/w) and AGE in a molar ratio of 1:1.5:3 (AGU: NaOH: AGE; theoretical  $DS = 3$ ). The used amount of sodium hydroxide was in accordance with earlier reported values of used sodium [11a] or potassium hydroxide [5c].

The influence of reaction temperature on the DS was not obvious under the applied conditions. The highest DS was obtained at 65°C and 85°C ( $DS = 1.5$  and  $1.3$ , respectively), though at 85°C a light brown discoloration of the reaction media was detected. Still higher temperatures appears to slightly reduce the DS ( $DS = 1.2$ ), probably due to hydrolysis of the ether bond under alkaline conditions [23]. The applied reaction temperature is

obviously dependent on the overall reaction conditions. *Bien* et al. [11a] and *Funke* et al. [5c] report elevated reaction temperatures up to 140°C, though employing 3.9 bar pressure and shorter reaction times (1–8 h) obtaining DS values similar to us. In this work the reaction temperature at 85°C was most favourable, despite the light discoloration, as the reaction media became more homogeneous compared to that at 65°C. *Huijbrechts* et al. reported recently a study on modification of waxy maize starch and amylase enriched maize starch by allyl glycidyl ether under mild conditions (44°C, 16 h) [11c]. However they used low concentrations of sodium hydroxide and allyl glycidyl ether with regard to AGU, striving for rather low degrees of substitution ( $DS = 0.2$ ). A similar procedure under mild reaction conditions is described in the patent literature [11b]. Also in this work low degrees of substitution ( $DS = 0.1$ ) were reported.

An efficient synthesis of alkyl-etherified starches must be catalyzed. The use of various sodium-based basic and weakly acidic compounds, e.g. sodium hydride, sodium hydroxide, sodium acetate or sodium formate has been reported [23]. Earlier investigations report the synthesis of alkylether-substituted starch with 1,2-epoxy alkanes using high pressure [11a] and temperature [5c, 11a] or prolonged reaction times up to 120 h under moderate temperatures using NaOH/Na<sub>2</sub>SO<sub>4</sub> as catalyst to obtain higher degrees of substitution and improved yields [11a]. *Funke* et al. studied the influence of potassium hydroxide concentration on the reaction efficiency of hydroxy-alkylation of starch by terminal alkyl epoxides [5c]. A reasonable DS was afforded even with rather low KOH concentrations (KOH: AGU; 0.4:1), however, the reaction temperature was 140°C. We varied the molar equivalent of sodium hydroxide from 1 to 2 with respect to the amount of used AGU, applying 85°C as reaction temperature for achieving a smooth paste-like reaction mixture. The DS was not increased by increasing the molar ratio of NaOH: AGU from 1:1 to 1.5:1. However, the higher sodium hydroxide amount produced a smoother reaction slurry. Increasing the NaOH: AGU ratio to 2:1 reduced the DS to 0.9. These results are in accord with those reported by *Bien* et al. [11a]. Apparently the reaction media became too alkaline and promoted the hydrolysis of formed ether bonds [23].

To obtain reasonably high DS-values ( $> 1$ ) requires excess use of the substituting reagent. In theory a DS-value (or more correctly molar substitution, MS, in case of epoxyalkanes) of three is obtained with a molar feed ratio of 1:1 of the epoxy reagent to hydroxyl groups in starch (equal to an epoxy reagent to AGU ratio of 3:1). *Huijbrechts* et al. showed that allyl glycidyl-modified starches can be atom-efficiently prepared [11c]. How-

ever, they only synthesized starches with rather low DS (DS = 0.2). *Teramoto et al.* [24] report a molar feed ratio 1:7.5 of hydroxyl groups of amylose to 1-bromopropane (i.e. AGU: Br-Pr, 1: 22.5) to achieve a completely substituted alkyl-etherified starch (DS = 3). *Bien et al.* [11a] obtained an alkyl-etherified starch with DS = 1.8 and DS = 2.4 using a ratio of AGU to 1,2-epoxyalkane of 1:3 and 1:5, respectively, within 4 h, though the reactions were performed at elevated pressure and temperature (3.9 bar and 140°C).

The effect of allylglycidyl ether concentration and reaction time on the DS was studied at 85°C employing a constant starch to sodium hydroxide ratio of 1:1.5. Reaction times between 16–24 h did not have a marked impact on the DS, resulting in molar substitutions slightly > 1 when applying a starch to AGE ratio of 1:3. Aiming for higher DS we increased the ratio of starch to AGE to 1:7. In this case, the reaction time had an obvious impact on the DS as seen in Tab. 2. Increasing the reaction time from 18 h to 24 h raised the DS from 1.9 to 2.3. A threefold molar excess of AGE to hydroxyl groups (AGU: AGE; 1:9) accomplished a close to total substitution (DS = 3) even within 14 h at 85°C.

### 3.2 FT-IR

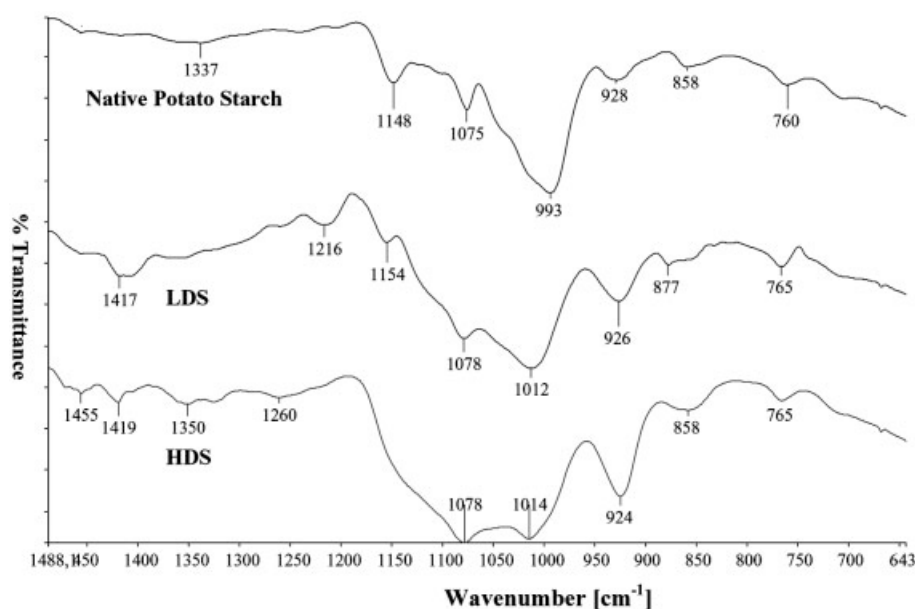
Fig. 1 shows the FT-IR spectra of native starch, LDS and HDS between 750 and 1370  $\text{cm}^{-1}$ . The absorption bands at  $\sim 930 \text{ cm}^{-1}$  and  $\sim 1080 \text{ cm}^{-1}$  was assigned to the C-C and C-O-C stretching and vibration, respectively, of starch and grafted AGE, and the peak at

$\sim 2900 \text{ cm}^{-1}$  was assigned to the C-H stretching vibration [25, 26]. The absorbances of LDS and HDS at  $\sim 930 \text{ cm}^{-1}$ ,  $\sim 1080 \text{ cm}^{-1}$  and  $\sim 2900 \text{ cm}^{-1}$  were all markedly increased as compared with those of native starch. The aforementioned absorption bands of HDS were obviously stronger than those of LDS. *Smits et al.* assigned absorbance bands at 1048 and 1022  $\text{cm}^{-1}$  to amorphous and crystalline regions, respectively [27]. Thermal analysis (DSC) suggests that both LDS and HDS crystallize but in the FT-IR the strong increase of the absorbance at 1078  $\text{cm}^{-1}$  hinders an unambiguous interpretation of any possible changes in the morphology. Unfortunately, we could not detect well resolved peaks for the allyl group at  $\sim 1600$ – $1750 \text{ cm}^{-1}$  and  $\sim 3050 \text{ cm}^{-1}$ , which would have been useful for comparison with the cured products [28].

### 3.3 $^1\text{H-NMR}$

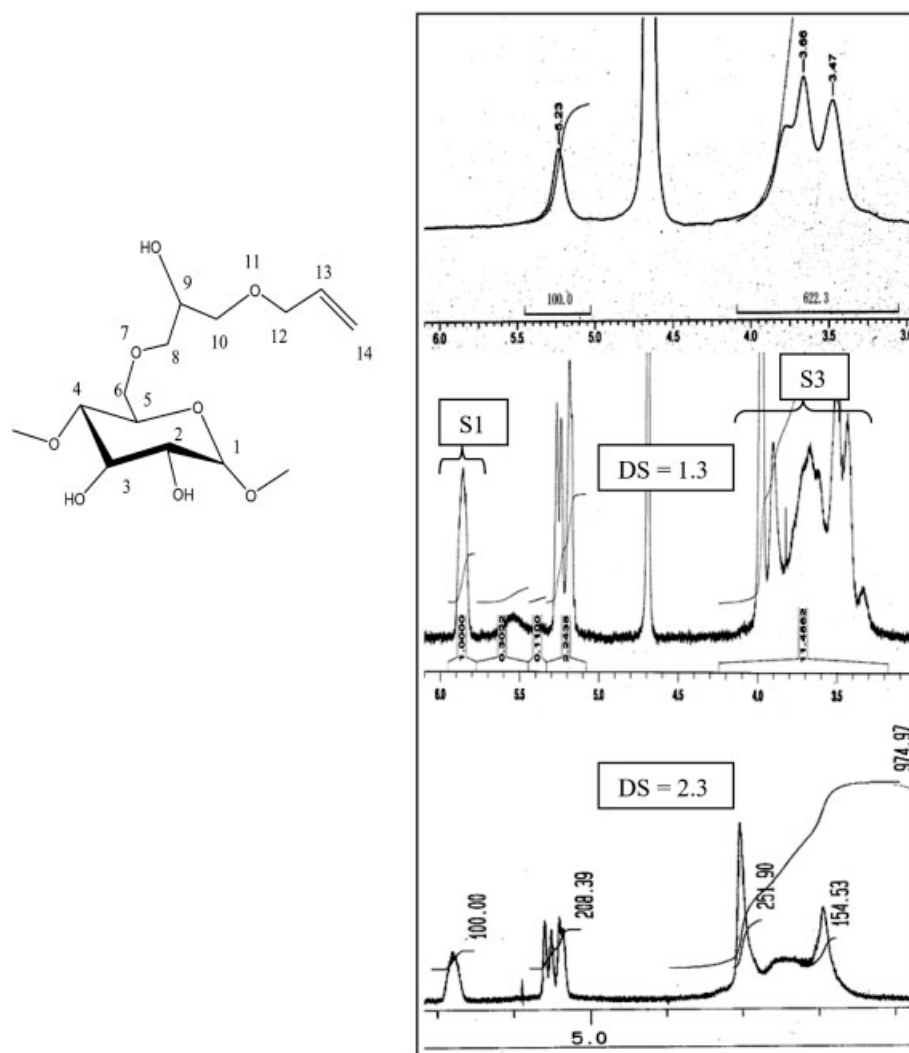
$^1\text{H-NMR}$  provides a simple, though rough, method to estimate the DS of AGE modified starch. The proton spectra of native starch, LDS and HDS, respectively, are shown in Fig. 2.

The DS was calculated by comparing the well resolved proton signal areas at 5.8 ppm and 3.25–4.10 ppm, defined as S1 and S3, respectively. The peak at 5.8 ppm originates from the methine proton of the AGE allylic double bond and the complex multiplet at 3.25–4.10 ppm arises from seven protons of AGE and six protons of AGU. Thus the DS can be calculated according to Equation (1).



**Fig. 1.** FT-ATR-IR spectra of native and AGE-modified starch. Upper IR spectrum shows native starch, the middle LDS (DS = 1.3) and lower HDS (DS = 2.3).





**Fig. 2.** Numbering and  $^1\text{H}$ -NMR spectra of native starch (upper right), and AGE-modified starch with low DS = 1.3 (middle) and high DS = 2.3 (lower).

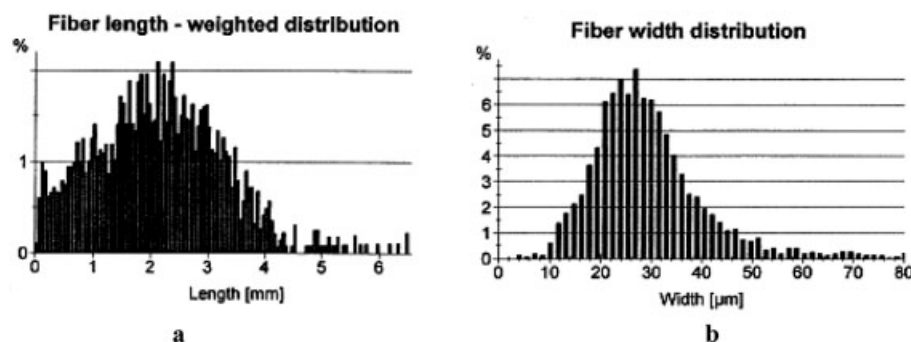
### 3.4 Composite preparation

AGE-modified starch with DS = 1.3 (LDS) and DS = 2.3 (HDS) was manufactured into wood-fibre reinforced thermoset composites using EGDA as crosslinker and BPO as initiator. The amount of crosslinker (EGDA) was adjusted to available allylic double bonds and was used in a molar ratio of 0.5:1 and BPO was applied in a constant 2% (w/w). The bleached softwood fibre content in the composites varied from 0 to 70% (w/w).

The distribution of the fibre dimensions were measured with a Kajaani Fibrelab equipment (Kajaani Electronic Ltd., Kajaani, Finland), as shown in Fig. 3. Even though the fibre length shows a considerable scatter, the fibres can be considered as long and slender, with an aspect ratio of approximately 100. Fibre degradation during processing can be neglected, because the fibres were treated gently during manufacture of the composites. Due to

the slenderness of the fibres, a reinforcing effect can be expected, in contrast to most wood-plastic composites where wood flour particles are used as filler. The latter tend to act as stress concentrations rather than reinforcements.

In the composite preparation, it was most important to produce homogeneous premixes of the modified starch, bleached softwood, crosslinker (EGDA) and initiator (BPO). It was extremely difficult to use dried AGE-starch or dry wood fibres for premix preparation. The EGDA crosslinker and BPO did not blend well, especially with the hydrophilic LDS, producing a rather heterogeneous granular substance into which it was very difficult to disperse the wood fibres. However, homogeneous premixes were obtained by excluding the drying step of the precipitated modified starch and using additional water/ethanol to mix the premix components. The premix was ready to be cured after solvent evaporation.



**Fig. 3.** Fibre length (a) and width distributions (b) of pure bleached softwood fibre samples, measured by Kajaani Fiberlab (Metso Automation) fibre length analyzer.

The premix was set into a steel mould which was placed into a press machine heated to 150–200°C. A pressure of 100 bar (according to the used Carver press machine) was applied for the HD-0 sample and 150 bar for the fibre-containing samples in order to form homogeneous composites. It was apparent that the LDS material had inferior flow properties than HDS. As seen from the SEM micrograph in Fig. 4A, the surfaces of the LDS samples have clear regions where fibres are not covered by starch, probably a consequence of high viscosity and too fast curing of the matrix. The HDS matrix produced composite samples with apparently even and flawless surfaces (Fig. 4B). The fibres are also well dispersed in the HDS matrix (Fig. 4C), and the modified starch evidently promotes a good wetting and interface to the fibres. The matrix has clearly been able to penetrate into the fibre lumen which should be beneficial in terms of limiting the composite water uptake. The lack of cracks propagating along fibre lines provides further evidence for a good compatibility between the matrix and fibre.

### 3.5 Thermal analysis

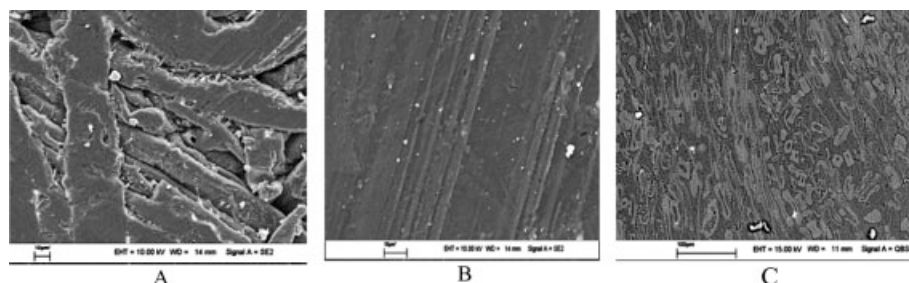
MDSC experiments enable a good separation of reversible and non-reversible thermal events and improve the resolution of closely occurring thermal events in biorelated materials [20, 29]. Thermal properties of starch and starch derivatives have been extensively studied by DSC. The available results are to some degree confusing and difficult to compare depending on the origin, chemical modifications and pretreatments of starch, the running conditions, the sample moisture content and the use of plasticisers. Fig. 5 shows the reversible and non-reversible heat flow thermographs of dry NS, LDS and HDS during heating (only one heating).

For all samples very broad endotherm signals starting at –30°C were observed during the reversible heat flow. The endotherm indicates some molecular transitions and it resembles the gelatinization in humid starch, although the samples were dried before analysis. At very close exam-

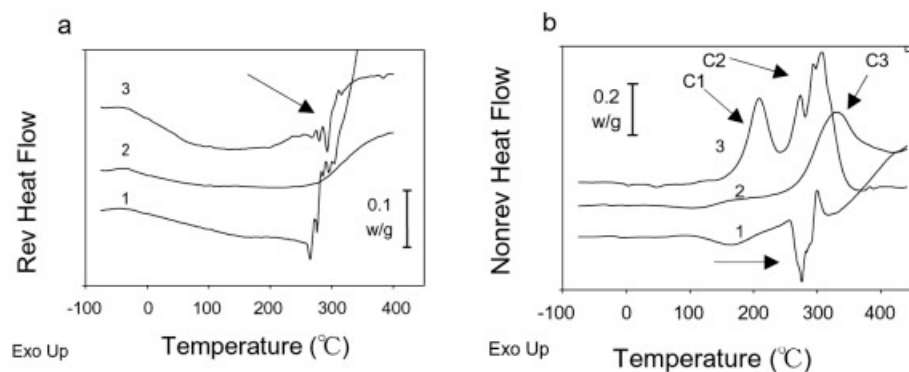
ination two small endotherms are visible at 0°C and 100°C representing melting and evaporation of water residues. An objective scrutinization revealed no obvious glass transition peaks. Possibly for HDS a change in heat flow at 47°C could be interpreted as a  $T_g$  (not shown). The endotherm signal of NS is evidently not as steep and the onset temperature is less obvious as compared with the slopes of LDS and especially HDS. The reduced hydrogen bonding ability in LDS and HDS, due to AGE-substitution, enhances their capability of macromolecular motion at energy absorption. The broad slopes apparently originate from the heterogeneous nature of the starch samples (traces of water, amylose vs amylopectin, AGE-substitution, polydisperse molecular weight). There is a detectable small endothermic signal at 280°C for HDS (Fig. 5A) demonstrating a tiny melting process.

Further evidence for more freely moving polymer chains at heating in HDS is found from the non-reversible heat flow thermogram (Fig. 5b) where two non-reversible exotherms C1 and C2 are detected for HDS at 200°C and 300°C, respectively, possibly indicating crystallization. We have not found earlier reports on such non-reversible exotherms for modified potato starch. Slow isothermal crystallization of amorphous waxy corn starch (amylopectin content > 99%, w/w) has been reported by *De Meuter et al.* [30]. *Fringant et al.* studied pea-derived amylose and amylopectin acetate and observed only for amylose acetate an exotherm at 250°C, which was confirmed as a crystallization process [31]. The origin of C1 and C2 is not clear to us and requires further analysis. Only a single exotherm C3 was observed for LDS at 300°C.

The non-reversible endotherm observed at 280°C for NS and the abnormally increasing base line of the reversible thermogram indicates decomposition of NS. This is in accord with degradation temperatures given in the literature [32]. No evident decomposition was observed for LDS and HDS according to their DSC thermograms. The increased thermostability of AGE-modified starch is in accord with earlier studies [32].



**Fig. 4.** SEM images of LDS-40 (A) and HDS-60 (B) samples surfaces and cross-section of a HDS-40 (C) showing the fibre distribution.



**Fig. 5.** (a) Reversible heat flow and (b) Non-reversible heat flow of dry native starch (NS) (1), LDS (2) and HDS (3) during heating. The arrow in 5a indicates the melt endotherm observed for HDS at heating, while the arrow-marked non-reversible endotherm for NS in 5b, is likely due to degradation.

The MDSC results imply that HDS actually is more pliable and acts less viscous at the composite processing temperature (150°C). The higher molecular motion and less viscous character in HDS is readily seen in the composite quality, where cured HDS composites exhibit a more homogeneous structure as compared with those of LDS.

### 3.6 Extraction

The cured samples were extracted under reflux in a Soxhlet-apparatus for 24 h. The LD-40 and LD-60 samples lost more weight after the extraction (Tab. 3) as compared with the corresponding HDS composites. The weight loss is probably the result of a less crosslinked matrix originating from problems to prepare a homogeneous premix of the more hydrophilic LDS starch matrix and the hydro-

phobic crosslinker. The HD-0 sample broke into small pieces during the extraction, making the weight loss measurement more difficult and inaccurate. The observed high weight loss for HD-0 is likely the result from small pieces escaping through the socket into the solvent as non-soluble material was recovered from the extraction solution. The truly dissolved matter was apparently quite small.

## 4 Conclusions

Allylglycidyl ether-modified starch was efficiently prepared with a low and high degree of substitution under moderate reaction conditions. Various premixes of AGE-starch, wood fibres and ethylene glycol dimethacrylate were prepared and cured by benzoyl peroxide under hot press conditions. MDSC analysis shows an increased thermal stability of the modified starch. Especially the high degree substitution-matrix (HDS) possessed melt flow properties suitable for composite preparation even with extremely high wood fibre contents up to 70% (w/w). The low degree substitution-matrix was less compatible with the EGDA-crosslinker and did not produce composite surfaces with equal good quality as those of HDS. The fibres were well distributed in the HDS matrix and good interfacial adhesion between the fibres and the HDS starch was

**Tab. 3.** Result of the extraction experiments.

Specimen	Weight before extraction [g]	Weight after extraction [g]	Weight loss [%]
LD-40	0.396	0.339	14.3
LD-60	0.397	0.348	12.3
HD-0	0.617	0.452	26.7
HD-40	0.378	0.378	0
HD-60	0.369	0.367	0.5



observed. Hygromechanical tests show that the HDS composites possess improved hygrostability, stiffness and strength [19].

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