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Allyloxy-modified starch with low degree of substitution for fiber reinforced thermoset starch composites

Jie Duanmu¹, E. Kristofer Gamstedt², Andrey Pranovich³ and Ari Rosling^{1*}

¹ Functional Materials Center, Laboratory of Polymer Technology, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo, Finland

² KTH Fiber and Polymer Technology, Royal Institute of Technology, Teknikringen 56, SE-100 44 Stockholm, Sweden

³ Laboratory of Wood and Paper Chemistry, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo, Finland

Abstract –In the present work dough moulding compound premixes of allyl glycidyl ether modified (AGE) -potato starch, (DS) =0.2, has been prepared and tested for its fiber reinforced composite properties. The AGE-starch was hydrolyzed with α -amylase under neutral condition for 6h at 45°C for improved process ability. The grafting and hydrolytic scission was confirmed by nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC), respectively. Homogeneous composite premixes of AGE-starch, wood fibers, various amount of glycerol and ethylene glycol dimethacrylate were successfully mixed with a Brabender-kneader at 55°C and cured by compression molding at 150°C using 2 wt% of dibenzoyl peroxide. Adding 5wt% of glycerol did not reduce the ultimate strength of the composites; 10% glycerol reduced the strength from 60 MPa to 40 MPa, and 16% glycerol to 14MPa. The results with 5 wt% glycerol are comparable with earlier achieved results. The water absorption rate increased with increased glycerol content and the mechanical strength of the composites was lost completely when the moisture uptake reached 15 wt%.

Keywords: A. Polymer-matrix composites, B. Mechanical properties, D. SEM, E. Heat treatment

1. Introduction

Starch is a macromolecular material of two structurally different polysaccharides, the linear amylose and the branched amylopectin, both of which are essentially 1, 4-linked α -D-glucan, with the latter in addition having branches to the main chain by 1, 6-linkages. Starch is inexpensive, renewable and there is consistent huge annual supply in the world. It has been considered as a very promising natural resource for biocomposites. Mixing starch with suitable plasticizers, we get a well known thermoplastic starch (TPS), which can be processed by conventional melt process technologies. Plasticizers are indispensable for the process of starch based biopolymers. They can form hydrogen bonds with starch, thus interrupting the strong bonding between hydroxyl groups of starch molecules and consequently decrease the viscosity of starch.¹⁻³ The properties of TPS depend much on the hydrogen bond-forming abilities between plasticizers and starch molecules. The most used plasticizers for starch are water, glycol and glycerol.^{2,3} In order to eliminate the disadvantages of starch plastics, such as water absorption and poor long-term stability, starch can also be chemically modified. Methods of chemical modification of starch, mainly include glucosidic bond cleavage (acid modification to dextrins)^{4,5}, forming new functional groups (carbonyl group formation during oxidation)^{6,7}, substitution of free available hydroxyl groups (by etherification or esterification)^{8,9}, and bridging of molecular chains by cross-linking reactions¹⁰. With an increased degree of modification the starch becomes more thermoplastic like and depending on the modification also more hydrophobic¹¹. In our previous work, a series of wood fiber

reinforced composites with high strength and stiffness were made from AGE-starch with a DS of 1.3.¹¹ In order to evaluate the potential of an even less modified and more environmentally-friendly material, the present work was undertaken to significantly reduce the DS of the AGE-starch and elucidate the new composite properties and their potential need for plasticization providing easy process ability by melt mixing. The composites were studied by scanning electron microscopy (SEM) for their microstructure and spatial fiber distribution, by three-point bending their ultimate strength and stiffness and their moisture uptake at 84.2% relative humidity. These tests showed that the low degree of substitution (DS=0.2) composites possessed half the ultimate strength and three quarters of the stiffness of similar composites made from the matrix with a degree of substitution = 1.3. The labels used to sign different samples are explained as following:

2. Experimental

2.1 Materials

Native potato starch was received as a gift from Lyckeby Stärkelse, Sweden. The enzyme, α -amylase (3000U/ml on Ceralpha Reagent at pH 6.0 and 40°C, Bacillus licheniformis) was from Megazyme, Ireland. Typical bleached kraft softwood pulp fibers were supplied by Imatra mill of StoraEnso, Imatra, Finland. All chemicals were used as received.

2.2 General procedure for synthesis and enzymatic hydrolysis of AGE modified starch with low DS =0.2 (D-LDS-0.5-6)

The method described in a previous work was used to synthesize and hydrolyze a different AGE-starch matrix.¹²

The used amount of AGE was decreased from 3:1 [AGE: AGU (anhydro-D-glucose)] to 0.5:1 (thus the new matrix is named LDS-0.5). A 25w% aqueous starch (40g) solution was pregelatinized for 1h under alkaline condition (1.5 equivalents NaOH per AGU) at 85 °C. To the solution, 3.66 ml of AGE (0.5 equivalents per AGU) was added while stirring and further reacted for 24h at 85°C. The reaction solution was cooled down to 45°C, the pH was adjusted to 6 with 0.1M HCl, after which 0.2ml of α -amylase (60 U/g native starch) was added, and the AGE-starch was hydrolyzed for 6h. The reaction was quenched, by deactivating α -amylase at 100°C for 10 min. The hydrolyzed D-LDS-0.5-6) was purified with 5×70 ml acetone (D-LDS-0.5 was precipitated in acetone and the acetone was decanted) and then dried in a vacuum oven (133 Pa) for 24h at 30°C. Dried D-LDS-0.5-6 was ground into powder and stored in a closed plastic bottle.

2.3 Composite preparation and curing

Benzoyl peroxide (BPO) to an amount of 0.1 g (2 wt %), 0.65 g ethylene glycol dimethacrylate (EGDA) (EGDA: allyl bond molar ratio, 0.5:1) and various amount of glycerol (0, 5, 10, and 16 wt% of the total premix weight) were placed into a 50 ml beaker and stirred to allow the BPO to disperse homogeneously into the mixture. After that, 5 g starch (D-LDS-0.5-6) was added to the beaker and the mixture was stirred to homogeneously. A Brabender kneader mixer, Rheomix 600 controlled with Haake

Rheocord 40 system was preheated to 50°C. Soft wood fiber (3.8 g) and the matrix mixture prepared above were placed into the mixer and mixed for 120 seconds at a rotating speed of 200 rpm. Of the final premix 0.4 g was placed into a steel mold, 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 for 10 min. Composite based on D-LDS-3-18 (AGE-starch with a DS= 1.3, degraded by α -amylase for 18 hours)¹² with 40w% wood fiber was also made with the same process for comparison.

2.4 Measurements

¹H NMR and degree of substitution

The starch was dissolved in deuterium oxide (0.5 wt %), and ¹H-NMR spectra were collected with a Bruker 500 MHz spectrometer. The proton spectra were referenced internally to the solvent signal of D₂O at 4.64 ppm. The following equation was used for a rough estimation of the AGE substitution degree by ¹H NMR

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

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 AGE unit.

Molecular weight

The molar-mass characteristics of the starch samples were determined by high pressure liquid chromatography equipped with a size exclusion column HPLC-SEC on an Agilent

1100 Series chromatograph equipped with Jordi Gel GBR Mixed Bed (Glucose) 250 mm x 10 mm ID + All-guardTM guard cartridge system with Jordi Glucose-DVB guard 7.5 mm x 4.6 mm ID (Alltech Associates Inc.). A miniDAWN Tristar multi angle laser light scattering MALLS detector by Wyatt Technologies and a Shimadzu RID-10A refractive index detector were used. The eluent was dimethyl sulfoxide (DMSO), and the flow rate 0.5 mL/min. Oven temperature was 50°C and Agilent 1200 Series G1329A auto sampler was used to inject solution 100mkl-200mkl. All samples were filtered through a 0.2 µm Teflon (PTFE) filter (VWR) prior to injection.

Scanning electron microscopy (SEM)

Composite samples were broken into half by pliers and the fracture surfaces from tensile side were viewed with LEO 1530 SEM working at an accelerating voltage of 15 kV. The fiber dispersion inside the composite was studied from the cut and polished (2400 grit silicon carbide paper) cross sections with SEM. Both the fracture surfaces and cross sections were coated with a thin layer of conductive carbon before microscopy.

Mechanical properties

Ten rectangular bars (12 mm × 3 mm × 3 mm) of each composite were manufactured. The machined surfaces were polished with 1600 grit silicon carbide paper. The test samples were conditioned at ambient condition at around 68% relative humidity (RH) for 1-2 weeks prior to the mechanical test.

Five specimens each were subjected to a three-point bending test in the in-plane direction and the out-of-plane direction, respectively.¹¹ A Minimat 2000 microtensile machine was used with a 200 N load cell. The processing method to manufacture disc-shaped composite plates induces in-plane random fiber orientationError! Bookmark not defined.¹⁴. The match-like specimens cut from the composites discs can thus be testing in bending in two different ways: in-plane loading or out-of-plane loading, also known edge-wise and flat-wise loading, respectively, for wood-based materials, sandwich structures and impact testing of short-fiber composites. The strength should differ for the two cases, since the crack is initiated at the surface of the machined edge in the case of in-plane loading, and at the flat surface in the case of out-of-plane loading. The difference basically relates to the effect of cut surface with cut incomplete fibers. The bending stiffness and both strength values have been characterized in this study.

The Young's modulus was calculated according Timoshenko beam theory with the following formula for in-plane loading:¹³

$$E = \frac{1}{C_b} \left[\frac{1}{4b} \left(\frac{L}{h} \right)^3 + \frac{\beta (1 + \nu)}{2b} \frac{L}{h} \right] \quad (4)$$

where $1/C_b$ is the slope of the linear part of the load versus midpoint deflection curves, b is the width of specimen, h is the height of specimen, L is the distance between the end supports, ν is the Poisson's ratio assumed to be 0.3, and β is geometrical factor assumed to 1.2 for rectangular cross sections. The ultimate strength was calculated from the three-point bending test as $\sigma = \frac{1}{2} Mh/I$, where the maximum moment is $M = PL/4$, and the second moment of area is $I = bh^3/12$. Furthermore, P is the applied load; h is the height of

the specimen, and b is the width of the specimen. Thus, both the bending strength and the Young's modulus (from bending test) can be determined based on the geometry of the specimen, the applied load and midpoint deflection, where the shear deformation is accounted for these relatively low aspect-ratio specimens.

2.3 Water vapour absorption and dimensional stability

For the water vapour uptake analysis, three disk-shaped samples ($\text{Ø } 12 \text{ mm} \times 3 \text{ mm}$) of each composite were dried at 50°C for 24 hours. The samples were conditioned at 84.2 % RH obtained with saturated KCl (aq) at room temperature. At predetermined points of time, the weight of selected samples was measured. Immediately before weighing, the surfaces of the samples were wiped with a tissue that absorbed the superficial free water. Five locations on each sample surface were selected to measure the thickness variation along with increasing time. Simultaneously, the transient diameter increase was measured for four positions. The average values of the dimensions and weight increase as a function of time of three specimens were calculated.

3. Results and discussion

3.1 Synthesis and Enzymatic degradation of AGE-modified starch

In this work, hydrolyzed AGE-starch with a DS as low as 0.2 was synthesized in alkaline aqueous media and composites based on the AGE-starch were made by melt mixing and hot compression molding as described in a previous work.¹² The less modified D-LDS-0.5-6 starch is evidently more hydrophilic compared to AGE-starch matrices with a

higher DS, and this was manifested by a more tedious drying and purification process of the D-LDS-0.5-6. The extent of AGE grafting was confirmed with ^1H -NMR. The DS was calculated comparing the well resolved proton signal area at 5.8 ppm originating from the methine proton of the AGE allylic double bond and the multiplet signal at 3.25-4.10 ppm which arises from seven protons of AGE and six protons of the AGU-unit¹⁴.

The α -amylase is the most common enzyme available for the digestion of starch. It is an endo-enzyme which catalyzes cleavage of starch molecule chains by hydrolyzing α -1-4 linkages at random sites. The susceptibility of starch to α -amylase attack is influenced greatly by the amount and distribution of substituent grafted on to starch via chemical modification.¹² Acetylated starch with DS of 1.5, 1.9 and 3.0 were proved not to be degraded by α -amylase from *Bacillus licheniformis*.¹⁵ Hydrolysis by starch-degrading enzymes is hampered more strongly by substitution at HO-2 than at OH-6.^{16,17} A 6-O-methyl glucose monomer protects only one adjacent glycosidic linkage from scission, whilst a 2-O-methyl glucose unit blocks two adjacent linkages.¹⁸

The lower degree of AGE-substitution reduced the sterical hindrance for α -amylase accessing scission sites in the starch backbone and the weight average molecular weight of LDS-0.5 (DS=0.2) was decreased from 70000 to 3000 g/mol (DP, i.e. number of glucose units, from 368 to 16) by 6 hours hydrolysis with α -amylase (Fig.2), while the weight average molecular weight of LDS-3 (DS=1.3) decreased from 500000 to 20000 g/mol (DP from 1448 to 58)¹² during same reaction conditions. The underlying reason for the big discrepancy in molecular weights between the original AGE-starches, 70 000 and

500000 g/mol for D-LDS-0.5 and D-LDS-3, respectively is unclear, though the final sodium hydroxide concentration is lower during the synthesis of LDS-3 matrix due to six times higher AGE amount and may thus cause this difference. Compared to D-LDS-3-6, the solubility of D-LDS-0.5-6 in DMSO was better and the quality of the SEC results was much improved.¹² The weight average molecular weight was calculated automatically by the software applying a $dn/dc=0.064\text{ml/g}$ for the DMSO based eluent.¹⁹

3.2 Composite preparation

Enzymatically degraded AGE-modified starches (D-LDS) with DS 0.2 (D-LDS-0.5) and 1.3 (D-LDS-3) were manufactured into wood fiber reinforced thermoset composites using EGDA as cross-linker and BPO as initiator. The amount of cross-linker (EGDA) was adjusted to available allylic double bonds and in a molar ratio of 0.5:1 and BPO was applied in a constant 2 wt% of D-LDS. The bleached softwood fiber content in the composites is 40 wt%.

The distribution of the fiber dimensions were measured with a Kajaani Fiberlab equipment and the results are shown in Fig.3. Even though the fiber length shows a considerable scatter, the fibers can be considered as long and slender, with an aspect ratio of approximately 100. Due to the slenderness of the fibers, 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. To retain fiber slenderness, a processing method that does not result in severe fiber length degradation should be used. This usually rules out injection molding and extrusion, but

speaks in favor of curing of premixes (cf. dough molding compounds) in hot-press molding, which is advocated in the present study.

In the composite preparation, it was most important to produce homogeneous premixes of the modified starch, bleached soft wood fiber, cross-linker (EGDA) and initiator (BPO). A homogeneous mix of the initiator BPO and cross-linker EGDA was first prepared manually. This mix was further blended with modified starch D-LDS until a seemingly homogeneous product was achieved. The mixture were stored for several hours to let the EGDA further diffuse into D-LDS before it was melt mixed with the fibers. High shear stress is a key factor for making thermoplastic starch²⁸ and we expect this to be the case also for the composites based on D-LDS-0.5 as the internal plasticization through the modification is limited due to the lower degree of substitution. In order to get high shear stress as to improve mixing during the melt mix, the rotating speed of the Haake Rheocord 40 was set to 200 rpm. A composite mixed at low shear stress (10rpm) was also made to compare the effect from shear. From Fig. 5a we can see the ultimate strength in 3-point bending being reduced by 100% comparing composites mixed at 200rpm (D-LDS-0.5-6-40M) with that mixed at 10 rpm (D-LDS-0.5-6-40M_10rpm).

3.3 Interface and fiber dispersion

From the cross-section of the melt mixed D-LDS-3-18-40M (matrix with DS=1.3) in Fig.4 B, one can see that fibers are homogeneously dispersed in the matrix, although the fibers are more flatter and the collapsed lumens are not that clearly visible as compared to the D-LDS-3-18-40 sample mixed in solution (Fig.4 A)¹². Although difficult to quantify, a fine dispersion was observed by microscopy for all cross-sections with no apparent

fiber bundles or agglomerates. For matrix systems composed of non-polar polymers with limited affinity to the fiber surface²⁰, the fibers tend to agglomerate and form cluster of fibres, which act as stress concentrations and reduce the strength of the composite. It is therefore desirable to avoid fiber agglomeration. In the present case, the fibers are well-dispersed in a water suspension, to which the starch has been added before the dewatering process. This assures a fine dispersion of fibers, despite their tendency to agglomerate under other circumstances. Such a procedure has also been successfully used to disperse wood-based microfibrils in a starch matrix²¹, which generally show an even stronger tendency to agglomerate than wood fibers. Decreasing the DS to 0.2, the matrix became softer and the cross-section of the composite (D-LDS-0.5-6-40M, Fig.4 C)) presented a waxy character and it became difficult to obtain a clear overview of the surface. After the cross-section was polished, it appeared that the fiber was covered with matrix and could not be observed directly due to smearing. Glycerol is a well known plasticizer for starch, however, when present in a low concentration, glycerol can produce an antiplasticizer effect and increase stiffness of glycerol/polymer mixture^{22,23}. There are two hypotheses for the phenomena; the plasticizer favors starch macromolecules to have increased mobility that facilitates packing of the starch polymers into crystal lattices²⁴, and strong interactions between the polymer and the plasticizer, producing a “cross-linker” effect at low concentrations in addition to possible crystallization²⁵. Due to a possible antiplasticization effect, the matrix D-LDS-0.5-6 with 5% glycerol was stiffer and the fiber traces could again be observed showing homogeneous dispersion in the cross-section (Fig. 4D). Increasing the glycerol content to 10% and 16%, the polished

cross section of composite showed once again a more waxy surface structure (Fig. 4 E and F).

The fracture surface of D-LDS-3-18-40 (melt mixed, Fig. 4H), was not as clean cut as the fracture surface of D-LDS-3-6-40M (solution mixed, Fig. 4G), however, the fibers are imbedded well in the matrix and no fiber pullout or fractured fibrils are visible. The effect from added glycerol is manifested from the SEM pictures of fractured surfaces (Fig 4 I-L). The fracture surfaces of the D-LDS-0.5-6 matrix with a DS of 0.2, without and with 5% glycerol, showed no fiber pull out. Though, the addition of 5% glycerol results in a more planar and brittle fracture surface. Further increasing the glycerol content caused marked fiber pull out and the horizontally oriented fibers became easily detectable (Fig 4 K and L). However, the pulled out fibers were still covered with adhering matrix, indicating that glycerol reduced the ultimate strength and especially the stiffness of the matrix, but the matrix still wetted the fibers well and the interface between fibers and matrix remained good.

3.4 Moisture absorption and dimensional stability

The inherent hydrophilic nature of starch is a key factor that limits the large-scale application of starch plastics and adding one of the most commonly used starch plasticizers, glycerol, makes starch plastics to absorb moisture even more and faster.²⁶

De Carvalho et al.²⁷ reported reduced tensile strength and elastic modulus for starch-glycerol-wood fiber composites with increasing glycerol contents measured at 97% RH.

They further observed that moisture uptake at saturation was reduced by addition of fiber

and reduction in glycerol content, though the fiber addition easily equalized the effect from glycerol addition. Even a 5 wt% of fiber addition did inhibit the impact of added glycerol on the moisture uptake, reducing the uptake of all composites to similar levels. In the present study, addition of glycerol did clearly increase the rate of vapor absorption at 83.2 % RH, definitely (Fig. 5a). The D-LDS-0.5-40M_16%glycerol showed the fastest water vapor absorption rate and saturation was reached at 40 hours. The saturation level for the glycerol free D-LDS-0.5-6-40M sample and those with 5 and 10 % glycerol, respectively, was not reached during the analysis as the test was interrupted at the point where the samples lost their integrity and started to dissolve. Though, one can clearly observe that the added glycerol resulted in an increased moisture absorption rate. The D-LDS-0.5-6-40M, D-LDS-0.5-6-40M_5%GLYCEROL and D-LDS-0.5-6-40M_10%GLYCEROL reached a 13% water vapor uptake at 50, 130 and 175 hours, respectively. We also compared the effect of composite premix preparation, solution vs. melt mixing, on the moisture uptake. D-LDS-3-6-40 prepared with solution mixing and D-LDS-3-18-40M prepared with melt mixing was compared during an immersion test, and we can detect that melt mixing not only decreased the water absorption rate, but also decreased the moisture saturation content from 16% to 11%. The reduced water sensitivity likely originates from a denser matrix-fiber structure formed during melt mixing excluding possible pores and debonded interfaces between fibers and the matrix, which was corroborated by the SEM analysis. We have earlier observed the neat cross-linked D-LDS-3-6-40 sample without fiber only absorbed maximum 1.5% moisture when immersed into water. This could suggest that the added fiber is more hydrophilic than the matrix or that the added fiber enhance water uptake due to a less dense structure with

higher porosity. Unfortunately we had to compare these two composites from two slightly different matrices, but based on our earlier work¹² we expect the D-LDS-3-6 and D-LDS-3-18 to behave rather similar with respect to their water uptake.

Surprisingly, all D-LDS-0.5-6 samples with and without added glycerol showed very low dimensional changes both in diameter (0.1-0.5%) and thickness (1-5%) directions (not shown) compared with those of D-LDS-3, 2% and 16%, respectively

3.5 Mechanical properties

The data obtained from the three point bending tests were reduced to Young's modulus and strength. The results are visualized in Fig. 6a-c. At low moisture content (equilibrium at ambient conditions of 60-70% RH), high shear stresses are essential for processing and mixing of starch based materials. Under high shear stress, full gelatinization of starch requires less water, and high shearing can thus improve the process.²⁸ From Fig 6a we can see that the ultimate strength of the sample prepared with 10 rpm (30 MPa) was 50% less than that of the sample prepared with 200 rpm (60 MPa), and further the corresponding Young's modulus was 40% less. The higher shear stress due to higher turning speed enhanced the mixing of pregelatinized AGE-starch and wood fiber. The strength of D-LDS-0.5-6-40M_5%glycerol was not improved compared to the uncured D-LDS-0.5-6-40M_5%glycerol_no BPO, indicating that the low cross-linking (DS=0.2) density do affect strength of the sample, though increasing the observed stiffness by 75% (Fig.6 a and b). A small degree of cross linking obviously improved the stress transfer ability and inherent stiffness of the cured matrix, resulting in a considerable increase in composite stiffness. Since the cross-linking density was low, the effect of fiber

orientation on the sample stiffness was more pronounced and the Young's modulus was higher in out-of-plane direction than in-plane direction (Fig.6 b and c)

A 5% glycerol addition showed an antiplasticization phenomenon and did not seemingly affect the ultimate strength and stiffness of the composite, possibly through a complexation with available hydroxyl groups on the starch chain and fiber²⁵. A further increase in glycerol content decreased the mechanical properties of the composite. The reduced properties due to glycerol addition might arise from a weakened matrix²⁹ and/or a poorer matrix/fiber interface³⁰. A 10% glycerol addition decreased the out-of-plane ultimate strength from 60 MPa to 40 MPa and 16% glycerol further decreased it to 14 MPa. Glycerol affected the stiffness even more than the strength. Ten percent glycerol decreased the in-plane direction Young's modulus from 3300MPa to 1500MPa; 16.7% glycerol decreased in-plane direction Young's modulus from 3300MPa to 200MPa.

Comparing the mechanical properties of D-LDS-3 based samples prepared by solution mix and melt mix (Fig.6 D-LDS-3-18-40 and D-LDS-3-18-40M), at ambient 60-70% RH, we can see that the ultimate strength and stiffness of the sample prepared by simpler and faster melt mix were around 20% higher than those of the sample prepared by the more tedious and cumbersome solution mix. A reduction in strength may derive from minute amount of water/solvent remnants in the composites prepared with by solvent assisted premix preparation. Though the melt mix procedure probably produce a more dense composite structure affording improved mechanical properties.

4. Conclusions

We have synthesized an allylglycidyl ether-starch with low DS of 0.2 and hydrolyzed it with α -amylase for 6 hours. Premixes of degraded AGE-starch, wood fiber and ethylene glycol dimethacrylate were prepared with melt mixing and cured by benzoylperoxide under hot press conditions. The reduced molecular weight improved the mixability and homogeneity of the premix and allowed a better matrix flow and wetting in compression molding, making it feasible to prepare premixes by melt mixing without glycerol as plasticizer.

The fibers were well distributed in the D-LDS-0.5-6 matrix and a good wetting of the fibers was observed by SEM. An addition of 5% glycerol did not affect the mechanical properties of the composites; however, higher glycerol concentrations reduced the strength and stiffness of the composites greatly and made the composites more hydrophilic absorbing moisture faster. The matrix of lower DS (0.2) was more water sensitive, absorbing more water than that of the higher DS of 1.3, and lost all its mechanical strength before its moisture content reached saturation. The simpler and less time consuming melt mixing method afforded more water resistant composites with higher ultimate strength and stiffness than those composites prepared with solution mixing method. This shows promise for development of dough or sheet molding compounds based on cellulose fiber reinforced thermosetting starch.

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Figure 1 ^1H NMR spectra of LDS-0.5 with a DS of 0.2

Figure 2 SEC chromatograms of native potato starch, LDS-0.5 and D-LDS-0.5-6 treated with α -amylase 6h.

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

Figure 4. SEM images of samples' (A-F) cross-section and (G-L) fracture surfaces showing the fibre distribution

Figure 5 (a) Weight and dimension ((b) thickness and (c) diameter variation at 83.2% humidity of D-LDS-0.5 composites and D-LDS-3 composites during immersion in water.

Figure 6 (a) ultimate strength in three-point bending, (b) out-of-plane and (c) in-plane Young's modulus of D-LDS starch with 40wt% fibre contents, in ambient (humidity: 60-70%)

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