UV Radiation of Cellulose Fibers and Acrylic Acid Modified Cellulose Fibers for Improved Stiffness in Paper

Mikaela Börjesson,[a] Gisela Richardson,[a] and Gunnar Westman [a,b,*]

In this study, the strength and stiffness was measured on paper sheets with and without acryl ester functionalization grafted with UV-reactive molecules. Three different monomers with one, two, and three UV-reactive groups, respectively, were reacted with the unsaturated ester. The tri-functional monomer had the most influence on the strength properties of the three monomers and was added in concentrations of 5 to 20 wt% of paper (0.03-0.11 mol eq./AGU). The strength and stiffness properties were measured with tensile tests. An increase in elongation, tensile index, and Young's modulus was seen after irradiation. However, the paper sheets esterified with acrylic acid prior to radiation showed no improvement in stiffness compared to a non-treated paper. As a result, the esterification with acrylic acid to enhance the grafting effect did not have the ability to compensate for the loss in strength caused by the esterification treatment.

Contact information: a: Chalmers University of Technology, Department of Chemistry and Chemical Engineering / Organic Chemistry, SE-412 96 Gothenburg, Sweden; b: Wallenberg Wood Science Center, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden;
* Corresponding author: westman@chalmers.se

INTRODUCTION

The world population is increasing, and as countries become developed this is normally accompanied by increased consumption. This puts increased demands on natural resources, and thus it becomes even more important to produce products from renewable raw materials. The demand for replacing non-renewable products with bio-based products requires knowledge and tools on how to utilize the resources in a more effective and sustainable way. In product areas wherein there are currently goods made from stone, metal, plastic, and glass it can be difficult to introduce bio-based materials. In other areas, wherein there is already a product share based on bio-based raw materials, it can be easier to introduce new bio-based materials and increase the percentage of bio-based products. Packaging is one area in which metal, plastic, and paperboard products are widely used. Within this area, paperboard has many advantages, such as good printability, low cost, and light weight. Compared to plastic packaging, it has some drawbacks, such as low deformability and poor resistance against liquids. For a liquid packaging made of paperboard, several layers of paper, plastics, and sometimes metals are used, where the paperboard is the thickest part of the packaging and also the part that gives the packaging its stability. The paperboard obtains its properties from the fiber network and type of cellulose fibers used. For paperboard, usually a multi-ply structure is employed with different layers of fibers having different properties. The cellulose fibers have several attributes, such as good biocompatibility, low cost, low density, high strength, good

mechanical properties, and worldwide availability. There are also some drawbacks, including poor dimensional stability, lack of thermoplasticity, high hydrophilicity, and poor crease resistance (Roy *et al.* 2009).

By changing the properties of the paperboard, the material can become more competitive against other materials. Increasing the strength and stiffness of cellulose fibers will increase the strength and stiffness of the final product, and less cellulose material will be needed to achieve the desired paperboard stiffness. A reduction in the amount of cellulose raw material used in packaging creates a lighter paperboard, which has environmental benefits such as in transportation.

Crosslinking of cellulose has been shown to increase the wet strength properties of paper because of stronger fiber-fiber joints in the fiber network (Xu *et al.* 2004; Horvath *et al.* 2010). Crosslinking or grafting of cellulose can be performed in different conditions, such as plasma treatment (Zubaidi and Hirotsu 1996), irradiation (Shukla *et al.* 1992; Chen and Wang 2006; Kumar *et al.* 2006), ionic grafting (Ikeda *et al.* 1988; Tsubokawa *et al.* 2000), and ring-opening reactions (Toledano-Thompson *et al.* 2005).

Electromagnetic radiation has been used in the industry since the early 1970s, and ultraviolet (UV) radiation has been shown to work successfully in curing applications on flat substrates (Glöckner *et al.* 2008). Today, UV radiation is the first choice for curing treatments because of its fast cure speed and the possibility of avoiding volatile organic compounds. Modified cellulose fiber systems that can be polymerized by UV radiation have been suggested for possible use in several fields, including hydrogels for contact lenses (Menashe 1986), general coating uses (Cook 1988; Cook and Simm 1998), and flame retardants in cotton fabrics (Gashti and Almasian 2013; Gashti *et al.* 2013). Acrylates, epoxides, and vinyl ethers are the most reactive functional groups during radiation treatment, and the backbone for irradiation crosslinking is preferably a polyester or polyether (Allen 1996).

Shukla and Athalye (1994) compared photo- and chemical-initiation techniques using different initiators and reaction parameters. The photo-initiation was performed by UV radiation; after optimization of the two techniques and different initiators, the photo-initiators turned out to give higher graft add-on values at lower temperatures and initiator concentrations compared to the chemical initiators. Pre-swelling of the cellulose fibers prior to grafting was also shown to have a positive effect on the graft add-on value (Shukla and Athalye 1992).

Crosslinking or grafting of cellulose by radiation treatment has been done by modifying carboxymethyl cellulose (CMC) and cellulose acetate through the addition of acrylic groups. The modified cellulose fibers are then polymerized using UV radiation, both through purely radical (Kumar *et al.* 2006) and metal-catalyzed (Chen and Wang 2006) reaction schemes. Böhm and co-workers (2013) introduced an approach for preparing functional paper in which they attached functional groups to cellulose microfibers by first absorbing poly(methyl methacrylate) (PMMA) copolymers to the paper substrate and then covalently binding to the substrate through UV radiation.

By first modifying the cellulosic fibers with functional groups suitable for crosslinking reactions, the crosslinking reaction can be controlled and the polymerization reaction will not start until treatment with heat or radiation occurs on the fibers. Controlled crosslinking of cellulose fibers by thermal treatment has been achieved by Hasani and Westman using the good leaving group characteristics of the N-methyl morpholinium substituent on modified cellulose fibers (Hasani and Westman 2011). Thermal treatment with the crosslinking agent 1,2,3,4-butanetetracarboxylic acid (BTCA) have been studied

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on both cotton substrates (Alimohammadia *et al.* 2012; Gashti *et al.* 2012) and kraft pulp fibers (Lund and Brelid 2014). Crosslinking through thermal treatment may be difficult to implement within the process line in the paper industry, whereas radiation treatment could be a better choice for possible implementation. We have therefore investigated how the strength properties in paper are affected by chemical modification and UV radiation. The strength properties were evaluated using tensile tests on paper strips. The paper used was modified with acrylic acid to give unsaturated ester groups on the cellulosic polymer. Three different monomers with one, two, and three UV-reactive groups, respectively, were polymerized with the unsaturated ester.

EXPERIMENTAL

Materials

Scandinavian dried softwood pulp obtained from Södra Cell AB was used for the study. The pulp was disintegrated at 30,000 revolutions of a PFI mill before use. Acrylic acid was purchased from Sigma-Aldrich.

The UV-reactive compounds N-(hydroxymethyl)acrylamide (HMAA), 1,6-hexanediol diacrylate (HDDA), trimethylol-propane triacrylate (TMPTA), and the photoinitiator 1-hydroxycyclohexyl phenyl ketone (HCHPK) were all purchased from Sigma-Aldrich and used without further preparation. The molecular structures of the monomers and photoinitiator are shown in Fig. 1.
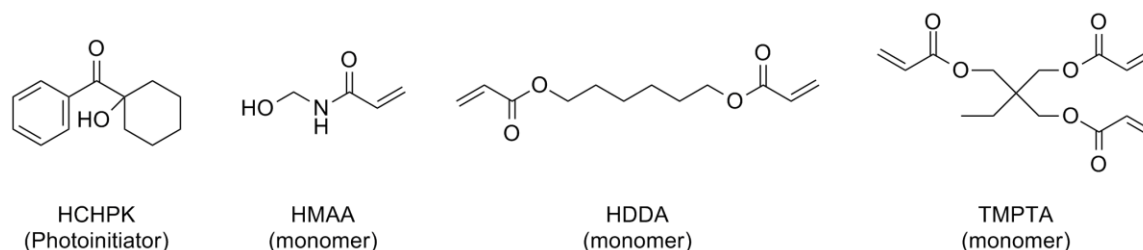

HCHPK
(Photoinitiator)

HMAA
(monomer)

HDDA
(monomer)

TMPTA
(monomer)

Fig. 1. Molecular structures of the photoinitiator (PI) and the three UV reactive monomers used in the study

Preparation of Handmade Paper Sheets

A semi-automatic Rapid Köthen sheet former designed for paper making was used to prepare handmade sheets with a basis weight of approximately 80 gm^{-2}.

Preparation of Cellulose Ester

The esterification between cellulose and acrylic acid (AA) has been investigated in an earlier study (Börjesson 2013). In the present study, acrylic acid (3 mol eq./AGU) was mixed with distilled water and sprayed on the surface of one side of the paper sheet to a dry content of 20% of the paper sheet.

The sprayed paper sheets were allowed to absorb the solution for 30 to 60 min before being heated in an oven at 160 °C for 60 min. After heating, the sheets were cooled down to room temperature.

Preparation of UV Radiated Sheets

A UV reactive compound and photoinitiator were added to the sheets before exposure to UV radiation. The HMAA monomer was added in concentrations of 20 wt% of the sheets (0.32 mol eq. HMAA/AGU), HDDA was added in 15 wt% of the sheets (0.11 mol eq. HDDA/AGU), and the TMPTA monomer was added in concentrations of 5 to 20 wt% of the sheets (0.03 to 0.11 mol eq. TMPTA/AGU). The photoinitiator was added in concentrations of 3 to 5 wt% of the sheets (0.024 to 0.04 mol eq. PI/AGU). To enhance the spread of the monomer/photoinitiator solution over the sheets, ethanol was added to the mixture and then allowed to evaporate before UV radiation. For UV irradiation a Black-Ray XX-15M UV Bench Lamp (15 W, λ =302 nm) was used at ambient temperature for 30 min, and the distance to the sample was 135 mm.

Characterization

Fourier-Transform Infrared (FTIR) spectrometry was used to analyze the esterification of the cellulose paper sheets. The FTIR was recorded on a Perkin Elmer Spectrum One instrument using the potassium bromide (KBr) pellet technique.

Tensile testing was performed on an Instron 5565A. Paper strips from sheets (gauge dimensions $50 \times 8.6 \times 0.2$ mm) were incubated at 23 °C and 50% RH for at least 24 h before testing. The strips were pulled at a strain rate of $17 \cdot 10^{-3}$ s^{-1}, corresponding to a cross-head speed of 0.85 mm s^{-1}, following the ISO standard 1924-3 (2005). Using the tensile test, strength properties such as tensile strain at max load (elongation), tensile stress at max load (tensile strength), and Young's modulus (stiffness) can be measured. The addition of a monomer/photoinitiator solution to the paper changed the basis weight of the sheets, and the tensile index was used as a measure of the inherent strength of the paper. The tensile index is the tensile strength (Nm^{-1}) divided by the basis weight (gm^{-2}).

Thermogravimetric analysis (TGA) was performed with a PerkinElmer TGA 7. Samples (two replicates) were heated at 5 °C min^{-1} under a nitrogen flow from 25 to 550 °C. The TGA was measured for both reference and AA-modified sheets, both UV-radiated and non-radiated. The UV-radiated sheets had an addition of 5 to 20 wt% TMPTA and 3 wt% PI. Weight losses were calculated from the TGA measurements and compared to the degree of grafting calculated from a graft add-on value (Shukla and Athalye 1992). The graft add-on values were calculated by the weight differences before and after UV irradiation (W_{graft}-W_0) divided by the weight of the sample before UV irradiation (W_0).

The water retention value (WRV) was measured for reference pulp samples and for AA-modified pulp samples, both UV-radiated and non-radiated. The WRV was measured on 200 mg of pulp soaked in water for 3 h and then centrifuged in Viva Spin tubes for 10 min at 3488 x g. The samples (three replicates) were weighed before and after oven drying at approximately 100 °C for 24 h. The WRV was calculated as the ratio of the difference in weight between the water-soaked sample and the dry sample (W_{wet}-W_{dry}) divided by the weight of the dry sample (W_{dry}).

Changes in the hydrophobicity of the paper sheets were studied using the Cobb test. The Cobb index was calculated using a Cobb tester and the procedure following the standard ISO 535 (1991). The Cobb index was measured for the UV-radiated non-treated reference sheets with the addition of 5 to 20 wt% TMPTA and 3 wt% of the photoinitiator. No replicates were performed.

Transmission electron microscope (TEM) samples were prepared by fixating paper samples in OsO$_4$ vapor for 2 h. Dehydration in 99.5% ethanol was followed by embedding in a TAAB low-viscosity resin (TLV). Thin sections of 70 nm were cut with an

ultramicrotome and stained according to the thiosemicarbazide-silver proteinate method described by Thiéry (1967). Images were taken with a LEO 906 E TEM at an accelerating voltage of 80 kV. TEM images were taken of the reference and the AA-modified sheets, both UV-radiated and non-radiated. The UV-radiated sheets had an addition of 20 wt% TMPTA and 5 wt% PI.

A scanning electron microscope (SEM) was used to examine the fiber surface structure of the UV-radiated paper sheets that had the addition of a monomer/photoinitiator solution (10 wt% TMPTA and 3 wt% PI) and compared to images of non-radiated paper sheets (both reference and AA-modified sheets). A LEO Ultra 55 FEG SEM operated at an accelerating voltage of 1.5 kV was used for the analyses.

RESULTS AND DISCUSSION

Preparation of Cellulose Acrylate Esters

The AA-modified cellulose sheets were analyzed with FTIR to estimate the formation of a carbonyl group caused by the esterification reaction. A new absorbance band, compared to the pure cellulose sample, at $v = 1725$ cm^{-1} was detected with FTIR, which showed an unsaturated cellulose ester and a successful esterification reaction. In previous studies reported by the authors' research group, the acrylic acid reaction on cellulose fibers was further evaluated (Börjesson 2013).

A suggested mechanism for the photo-grafting polymerization of TMPTA and cellulose are shown in Fig. 2. There was a transition of the carbonyl group in the photoinitiator when exposed to UV light within its absorption area. The radical form of the photoinitiator can get protonated if a hydrogen in an aliphatic carbon is close enough. New radical species are formed which can give new formation of carbon-carbon bonds. The photochemical attachment of polymer chains will continue on both cellulose fibers and within the polymer itself (Yibing *et al.* 2006; Böhm *et al.* 2013).

Tensile Tests on Paper Sheets

The strength and stiffness of the paper sheets were measured with a tensile test. Heating and washing the paper affected the strength of the sheets (Table 1, no. 1 compared to no. 2). The paper sheets used as reference for the modified samples were treated the same way as the AA-modified sheets but without reagent. A tensile test of the AA-modified sheets showed lower strength properties than the reference samples (Table 1, no. 2 compared to no. 3). The decrease in strength properties of the AA-modified sheets might be due to acid hydrolysis of the cellulose fibers during the esterification reaction (Gurnagul *et al.* 1992; Berggren *et al.* 2001).

Three different UV reactive compounds were tested; HMAA, HDDA, and TMPTA (Fig. 1). The tri-functional monomer, TMPTA, showed the highest increase in strength properties (Table 1, no. 4-6) and was the only monomer that was used for further evaluation.

Different amounts of TMPTA and 3 wt% PI were added to non-treated reference sheets before UV radiation (Table 1, no. 7-10). The optimum concentration of TMPTA for the maximum increase in tensile index was between 10 and 15 wt% (Table 1, no. 8 and 9), which gave a tensile index value that was twice as high as in the non-radiated sample (Table 1, no. 1 compared to no. 8).
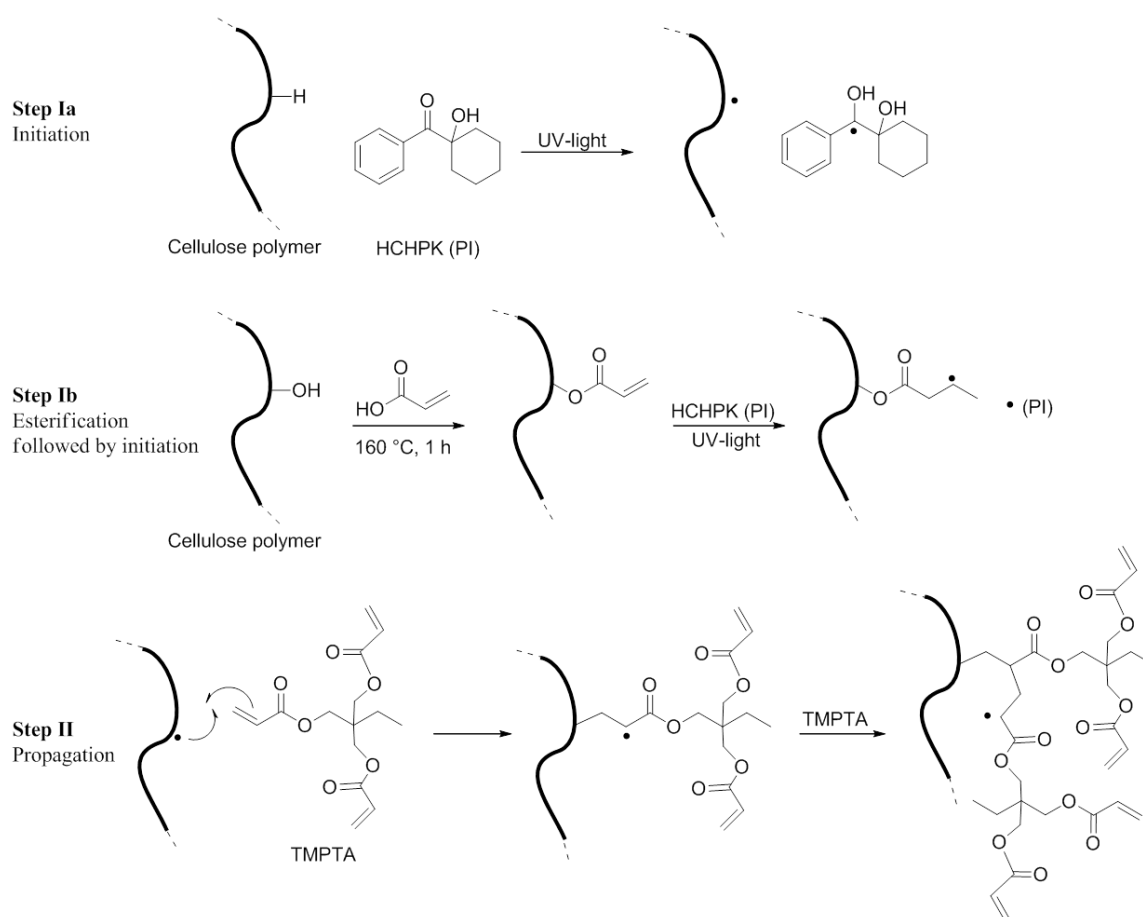
Fig. 2. A suggested mechanism of the photo-grafting polymerization of TMPTA with cellulose fibers. Step Ia shows the initiation mechanism for a non-treated cellulose fibers and step Ib shows the esterification with acrylic acid followed by an initiation step. Both step Ia and Ib are followed by propagation showed in step II, here illustrated by the non-treated cellulose fiber.

For the acrylic acid-modified sheets with the addition of different amounts of TMPTA and 3 wt% PI (Table 1, no. 11-14), the optimum concentration of TMPTA for the maximum increase in tensile index was 5 wt% (Table 1, no. 11). The maximum tensile index increase was four times higher in the UV radiated AA-modified paper sheet than in the non-radiated AA-modified paper sheet (Table 1, no. 3 compared to no. 11).

Despite the high increase in strength found in the UV-radiated, AA-modified paper sheets, the strength properties were not higher than in the non-treated reference sheets (Table 1, no. 1 compared to no. 11), which means that the acrylic-acid modification might enhance the crosslinking of the cellulose fibers, but the modification cannot compensate for the weakness the acidic hydrolysis causes.

No other functionalization of cellulose fibers was performed in the study since the strength properties of a UV radiated paper sheet was improved when performed on the non-treated reference sheets.

Table 1. Elongation, Tensile Index, and Young's Modulus for Reference and AA-Modified Paper Sheets Treated with Different Concentrations of Monomer Before UV Radiation

No.	Sample	Elongation (%)	Tensile index (Nmg^{-1})	Young's modulus (MPa)
1.	Reference sheets (nt; non-treated)	2.12 (0.09)	27.54 (0.81)	1842 (109)
2.	Reference sheet (washed)	1.74 (0.23)	18.49 (0.88)	1055 (90)
3.	Acrylic acid (AA) modified sheet	1.45 (0.07)	6.29 (0.07)	395 (5)
4.	AA-mod. sheet + 20 wt% HMAA (0.32 mol eq. HMAA /AGU)	2.26 (0.08)	10.46 (0.35)	339 (17)
5.	AA-mod. sheet + 15 wt% HDODA (0.11 mol eq. HDDA /AGU)	2.21 (0.21)	9.88 (0.80)	373 (10)
6.	AA-mod. sheet + 20 wt% TMPTA (0.11 mol eq. TMPTA/AGU)	1.77 (0.15)	15.87 (0.35)	858 (128)
7.	Ref. sheet (nt) + 5 wt% TMPTA (0.03 mol eq. TMPTA/AGU)	4.50 (0.66)	49.44 (1.58)	1983 (55)
8.	Ref. sheet (nt) + 10 wt% TMPTA (0.05 mol eq. TMPTA/AGU)	5.54 (0.38)	58.92 (1.37)	2109 (45)
9.	Ref. sheet (nt) + 15 wt% TMPTA (0.08 mol eq. TMPTA/AGU)	5.42 (0.54)	57.36 (3.05)	2106 (118)
10.	Ref. sheet (nt) + 20 wt% TMPTA (0.11 mol eq. TMPTA/AGU)	4.41 (0.43)	47.27 (0.70)	1928 (138)
11.	AA-mod. sheet + 5 wt% TMPTA (0.03 mol eq. TMPTA/AGU)	2.77 (0.29)	25.17 (1.28)	1014 (48)
12.	AA-mod. sheet + 10 wt% TMPTA (0.05 mol eq. TMPTA/AGU)	2.67 (0.22)	23.43 (3.06)	871 (33)
13.	AA-mod. sheet + 15 wt% TMPTA (0.08 mol eq. TMPTA/AGU)	3.17 (0.16)	22.02 (0.46)	890 (28)
14.	AA-mod. sheet + 20 wt% TMPTA (0.11 mol eq. TMPTA/AGU)	1.77 (0.15)	15.87 (0.35)	858 (128)

nt = non-treated reference sheets
Standard deviations are shown in brackets

TGA Measurements

Thermogravimetric analyses of sheets (non-radiated and UV-radiated) were compared for both reference (Fig. 3a) and AA-modified samples (Fig. 3b). Differences between UV-radiated paper and non-radiated paper were seen, and a new decomposition region was found at approximately 400 to 500 °C for the UV-radiated paper samples. A sample with only the monomer/photoinitiator solution that has been exposed for UV radiation was analyzed with TGA and showed a decomposition temperature near 500 °C (dotted line in Fig. 3a and 3b). The new decomposition region found in the UV-radiated paper samples is due to the grafting between cellulose and TMPTA. The weight loss for the new decomposition region between ca 400 and 500 °C could be determined and the weight losses for the different samples are shown in Table 2. Because the decomposition of the cellulose was similar in both non-radiated and radiated samples, it can be assumed that the grafting was located at the surface of the fibers.

Table 2 shows the calculated graft add-on value based on the weight changes between a grafted paper and a non-grafted paper and the weight loss determined from the TGA measurements for the new decomposition region between *ca.* 400 and 500 °C. Similar trends between the graft add-on values and the weight losses can be seen, and generally the

more TMPTA added, the higher degree of grafted material. From the weight loss measured by TGA in Table 2, it can be seen that the grafted amount in the reference (nt) sample with 15 wt% TMPTA added (0.08 mol eq. TMPTA/AGU) was similar to the reference (nt) sample with 10 wt% TMPTA added (0.05 mol eq. TMPTA/AGU) and the maximum stiffness increase in the tensile test measurements was between 10 and 15 wt% for the non-treated reference samples. The maximum stiffness increase for the UV-radiated, AA-modified sheets were for the paper with 5 wt% TMPTA (0.03 mol eq. TMPTA/AGU) added, which corresponds to a graft add-on value of 12.38% (Table 2). From the results in Table 2 together with the results from the tensile test in Table 1, it seems like approximately 11 to 12% grafted material gave the highest stiffness increase.
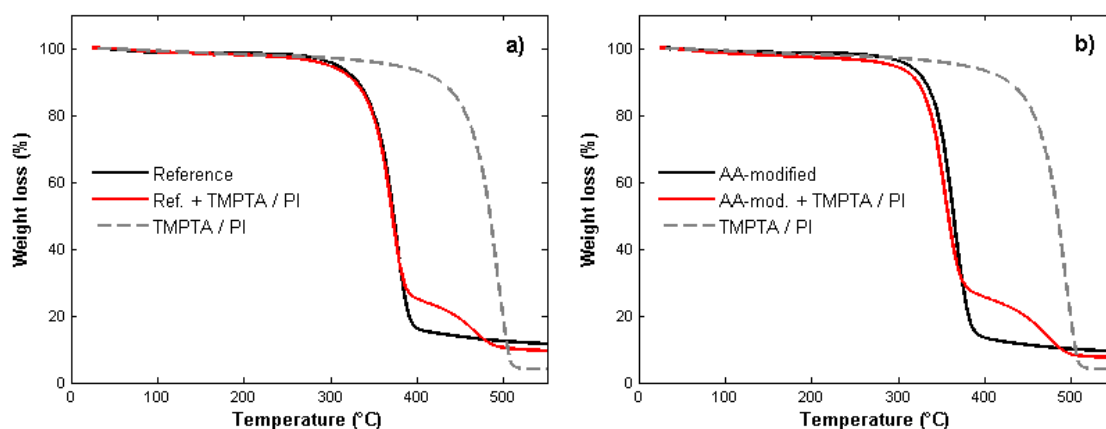

Fig. 3. TGA curves for a) reference paper sheets and b) AA-modified paper sheets. The dotted line to the right in both figures is the monomer/photoinitiator solution alone that has been exposed for UV radiation.

Table 2. Weight Loss (%) for the Decomposition Area Between 400-500 °C from the TGA Measurements and the Graft Add-On Values Calculated from the Weight Changes Between Grafted and Non-Grafted Paper

Sample	Graft add-on value (%)	Weight loss (%) at 400-500 °C
Reference (nt) + 5 wt% TMPTA (0.03 mol eq. TMPTA/AGU)	6.74 (1.21)	8.54 (0.60)
Reference (nt) + 10 wt% TMPTA (0.05 mol eq. TMPTA/AGU)	11.72 (0.43)	12.89 (0.07)
Reference (nt) + 15 wt% TMPTA (0.08 mol eq. TMPTA/AGU)	15.96 (1.16)	11.86 (1.08)
Reference (nt) + 20 wt% TMPTA (0.11 mol eq. TMPTA/AGU)	15.84 (0.73)	15.38 (0.50)
AA-mod. + 5 wt% TMPTA (0.03 mol eq. TMPTA/AGU)	12.38 (0.57)	11.07 (0.01)
AA-mod. + 10 wt% TMPTA (0.05 mol eq. TMPTA/AGU)	16.57 (0.67)	15.98 (1.84)
AA-mod. + 15 wt% TMPTA (0.08 mol eq. TMPTA/AGU)	22.21 (0.52)	13.26 (1.06)
AA-mod. + 20 wt% TMPTA (0.11 mol eq. TMPTA/AGU)	26.53 (0.48)	18.22 (3.41)

Standard deviations are shown in brackets

Water Retention and Absorption Measurements

AA-modified samples (Table 3, no. 7-11) had lower WRV compared to the washed reference samples (Table 3, no. 2-6), which indicates structural changes resulting from the esterification reaction. The WRV was lower in all the UV-radiated samples that had been treated with different amounts of TMPTA and 3 wt% PI. The WRV decreased with increasing amounts of TMPTA added which corresponds to the amount of grafted material presented in Table 2. The reduction in WRV was expected; as for the tensile test results, the non-treated (nt) reference sample had a higher value than the washed reference sample because of the loss of fines and small fiber fragments after the washing (Table 3, no. 1 compare to no. 2). Loss of fines and small fiber fragments gives a lower interaction with water and therefore also a lower WRV.

The reduction in WRV for the AA-sample compared to the reference sample is due to the acrylic acid esterification reaction, where some of the hydroxyl groups on the cellulose polymer have been substituted with ester groups, which decrease the interaction between cellulose and water.

Table 3. WRV for UV-Radiated Pulp with Different TMPTA Concentrations of 5 to 20 wt% of Pulp (0.03 to 0.11 mol eq. TMPTA/AGU) and 3 wt% of a Photoinitiator (0.024 mol eq. PI/AGU).

No.	Sample	WRV	% water in sample
1.	Reference (nt)	1.110 (0.01)	52.5 (0.2)
2.	Reference (washed)	0.672 (0.05)	40.2 (1.7)
3.	Reference (washed) + 5 wt% TMPTA (0.03 mol eq. TMPTA/AGU)	0.641 (0.06)	39.0 (2.3)
4.	Reference (washed) + 10 wt% TMPTA (0.05 mol eq. TMPTA/AGU)	0.618 (0.03)	38.2 (1.2)
5.	Reference (washed) + 15 wt% TMPTA (0.08 mol eq. TMPTA/AGU)	0.589 (0.01)	37.1 (0.4)
6.	Reference (washed) + 20 wt% TMPTA (0.11 mol eq. TMPTA/AGU)	0.520 (0.01)	34.2 (0.4)
7.	AA-sample	0.537 (0.02)	35.0 (0.8)
8.	AA-mod. + 5 wt% TMPTA (0.03 mol eq. TMPTA/AGU)	0.529 (0.02)	34.6 (0.8)
9.	AA- mod. + 10 wt% TMPTA (0.05 mol eq. TMPTA/AGU)	0.501 (0.02)	33.4 (0.9)
10.	AA- mod. + 15 wt% TMPTA (0.08 mol eq. TMPTA/AGU)	0.493 (0.01)	33.0 (0.5)
11.	AA- mod. + 20 wt% TMPTA (0.11 mol eq. TMPTA/AGU)	0.498 (0.04)	33.2 (1.9)

nt = non-treated reference sheets
Standard deviations are shown in brackets

The hydrophobicity of the UV-radiated non-treated paper sheets with the addition of different amounts of TMPTA and 3 wt% PI was studied using a Cobb test. As expected, the Cobb index of radiated sheets decreased as more TMPTA was added to the paper sheets (Table 4). A lower Cobb index means more hydrophobic paper, and the results in Table 4 correspond to the WRV results in Table 3.

Table 4. Cobb Index for UV-Radiated Non-Treated Reference Sheets with 5 to 20 wt% TMPTA Added (0.03 to 0.11 mol eq. TMPTA/AGU) and 3 wt% of a Photoinitiator (0.024 mol eq. PI/AGU)

Sample	Cobb index
Reference (nt)	222.8
Reference (nt) + 5 wt% TMPTA (0.03 mol eq. TMPTA/AGU)	151.8
Reference (nt) + 10 wt% TMPTA (0.05 mol eq. TMPTA/AGU)	86.5
Reference (nt) + 15 wt% TMPTA (0.08 mol eq. TMPTA/AGU)	97.8
Reference (nt) + 20 wt% TMPTA (0.11 mol eq. TMPTA/AGU)	33.5

Microscopic Analyses of the Fiber Structure

TEM analyses of AA-modified sheets and reference sheets showed that the surface of the fibers had changed. The unsaturated ester bonds as well as TMPTA were stained using OsO_4 fixation, which can be seen on the surface of the fibers as darkened areas. The AA-modified fiber (Fig. 4b) shows a darkened area located on the surface of the fibers, which cannot be seen in the reference sample (Fig. 4a). The darkening was due to the esterification reaction with acrylic acid. Figures 4c and 4d show a reference fiber and an AA-modified fiber, both with 20 wt% TMPTA and 5 wt% PI added and exposed to UV radiation for 30 min. In both figures, a darkened area on the fiber surface was apparent, similar to a thin film, which smoothed out the roughness of the fibers. As expected, for the UV-radiated TMPTA treated fibers the polymer film was thicker.
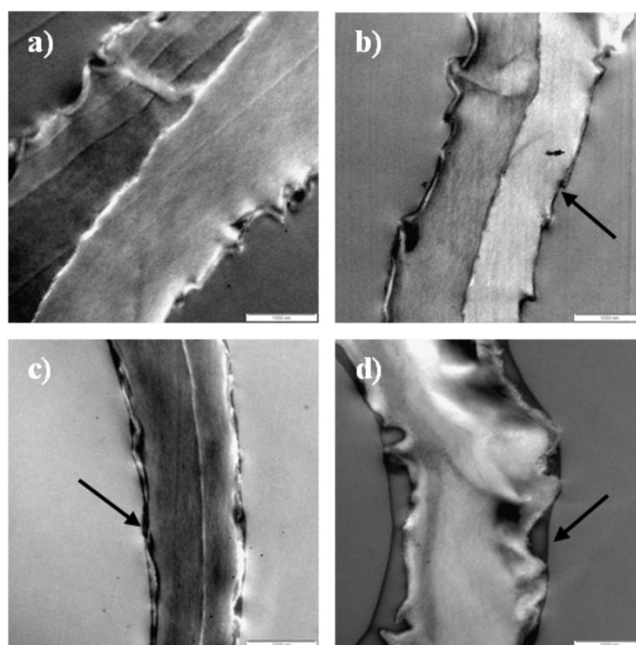

Fig. 4. TEM images of cellulose fibers stained with OsO_4: a) reference, b) AA-modified, c) reference + TMPTA (UV-radiated) and d) AA-modified + TMPTA (UV-radiated)

SEM images of the fiber surface network showed no significant differences between non-radiated and UV-radiated AA-modified paper samples (Fig. 5a and 5b). However, the non-treated reference sample (Fig. 5c) consisted of more fines and small fiber fragments in between the long fibers compared to the AA-modified sample. A similar

difference in fiber structure was seen between non-treated reference sample and a UV-radiated sample with 10 wt% TMPTA and 3 wt% PI added, probably caused by the addition of the monomer/photoinitiator solution. The decrease or reorientation of small fiber fragments could be the explanation to the decrease in strength properties between a washed paper and a non-treated paper that was seen in Table 1 (no. 1 compare to no. 2), since fines and small fiber fragments in between the long fibers cause more fiber joints in the network, which increased the strength properties (Xu *et al.* 2004; Horvath *et al.* 2010). At higher magnification, the fiber joints of the UV-radiated reference sample (Fig. 5f) appeared to be more stuck together than in the non-treated reference sample (Fig. 5e). Strong fiber joints increased the strength properties, as seen in the tensile test (Table 1).
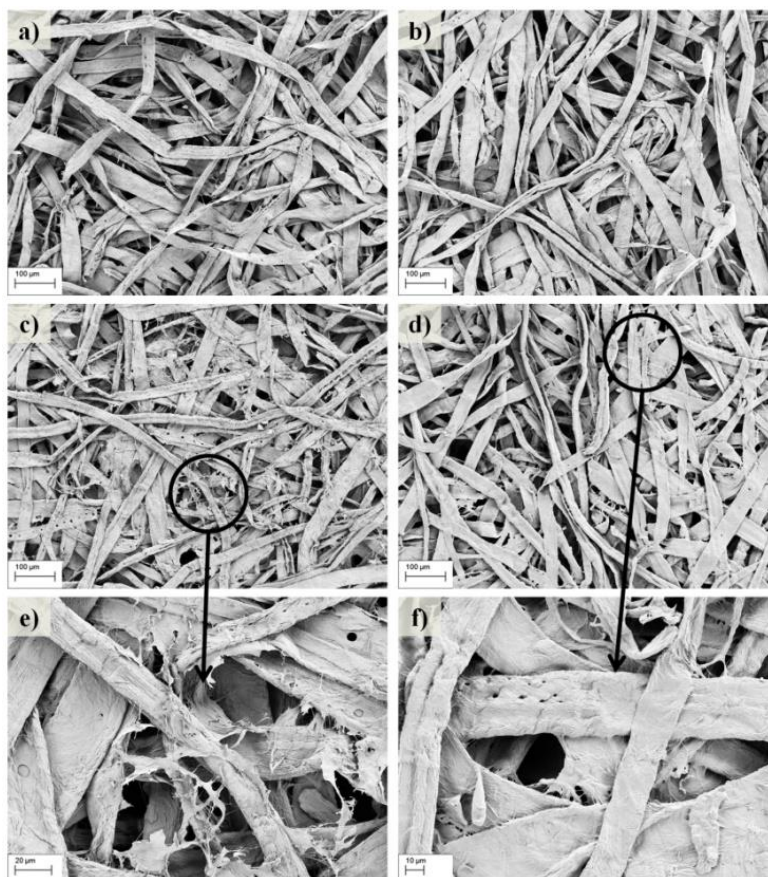

Fig. 5. SEM images of paper sheets: a) AA-modified, b) AA-modified + TMPTA (UV-radiated), c) reference (nt), d) reference (nt) + TMPTA (UV-radiated), e) reference (nt) (higher magnification), and f) reference (nt) + TMPTA UV-radiated (higher magnification)

CONCLUSIONS

1. The acrylic acid esterification of cellulose fibers and washing steps affected the strength properties of the fibers and the reorientation of small fines, which was seen in the tensile test, the WRV, and in the SEM images. Crosslinking by radiation of the acrylic acid esterified paper did not have the ability to compensate for the loss in strength caused by the esterification treatment due to heating, washing, and acid hydrolysis.

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2. The UV-radiated non-treated paper sheets showed the highest value in strength properties, with a tensile index double that of the non-radiated sheets (10 wt% TMPTA added corresponding to 0.05 mol eq. TMPTA/AGU and 12.89% grafted amount according to TGA measurements). Acrylic acid modified sheets showed an increase in the tensile index that was four times higher than in the non-radiated, AA-modified sheets (5 wt% TMPTA added corresponding to 0.03 mol eq. TMPTA/AGU and 11.07% grafted amount according to TGA measurements). Despite the high increase in the tensile index, the UV-radiated, AA-modified sheets were weaker than the non-treated paper sheets.

3. The amount of grafted material from the TGA measurements and the calculated graft add-on value together with the tensile test results shows that an approximately 11 to 2% grafting amount gave the highest increase in elongation, tensile index and stiffness.

4. TGA and microscopic analyses of the fiber structures showed that the treatment of the fibers took place on the fiber surface. WRV measurements and the Cobb index showed an increase in the hydrophobicity of the UV-radiated samples compared to non-radiated samples.

5. Three different UV reactive compounds were tested, and the tri-functional monomer, TMPTA, was the most suitable for increasing strength properties. TMPTA is FDA-approved, which makes it suitable for UV radiated paperboard in packaging applications for food products.

ACKNOWLEDGMENTS

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