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Preparation of superabsorbent cellulosic hydrogels

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ABSTRACT

In this work, milled softwood (SW) bleached kraft fibers were crosslinked by esterification with poly(vinyl methyl ether-co-maleic acid) (PVMEMA) and polyethylene glycol (PEG). The effects of fiber length, crosslinking reaction time, and dosage of PVMEMA on water absorption and retention value (WAARV) for the crosslinked fibers were determined. The results show that as the softwood fiber length is mechanically decreased from 2.41 to 0.50 mm and employing a weight ratio of fiber to polymers equivalent to 1.00:1.28 the WAARV increased from 86.50 to 189.20 g/g. Analysis of the crosslinked fibers by SEM and light microscope indicated that the polymers and fibers form a crosslinked fibrous matrix. FT-IR spectroscopy was employed to detect the ester linkage between PVMEMA and PEG/SW kraft pulp fibers. The results suggested that the ester crosslinked pulps exhibit excellent water absorbent properties and have the potential of utilizing milled bleached SW kraft fibers, such as refiner dust or pulp fines, for novel water absorbent applications.

1. Introduction

Conventional bleached kraft pulps are frequently used in a host of water absorbing product applications typically absorbing water approximately 20 times their weight (Matushek, 2008). However for a variety of applications, cellulosic materials are being replaced by superabsorbent polymers (SAP) and these hydrogels are widely being used for diapers, hygiene products, and related applications. SAP absorbs water through hydrogen bonding with the water molecules and due to osmotic pressure (Kabiri, Omidian, Hashemi & Zohuriaan-Mehr, 2003). Most SAPs are prepared by aqueous phase polymerization of acrylic acid in the presence of a crosslinking monomer and an initiator. For some industrial applications acrylamide is also used as a co-monomer (Burridge, 2005). Charge neutralization of the acid groups is accomplished with base either pre- or post-polymerization depending on the type of reactor and reaction conditions (Burridge, 2005). Typical acrylic acid-based superabsorbent polymers will absorb water up to a 1000-fold of their weight (Buchholz, 1994).

The production and cost of acrylic acid-based SAP are strongly dependent on petroleum derived chemical feedstocks. The partial and/or complete replacement of petroleum-based chemicals with their equivalent based from renewable bio-based resources is a growing international effort that will only continue to accelerate in the future (Pu, Zhang, Singh & Ragauskas, 2008; Ragauskas et al., 2006; Stocker, 2008). Cellulose is one of the most abundant biopolymers provided by nature and its utilization for assorted applications has seen a renaissance in research and development. The functionalization of cellulose is a common approach to impart improved or new physical properties. Several researchers have studied the grafting of polycarboxylic acids onto cellulose fibers to increase the wet strength of wood pulp paper. For example, Xu and Yang (1999), Yang and Xu (1998) and Yang, Xu and Wang (1996) grafted poly(maleic acid) onto wood pulp cellulose and thermally cured the wood fibers, improving both wet strength and dimensional stability of paper. Xiao and Meshitsuka synthesized high-retention water absorbents from kraft pulp by introducing carboxymethyl groups onto hardwood pulp and then crosslinking the pulp with polyethylene glycol diglycidyl ethers. By this process, the water retention values of the modified pulp could achieve up to 500 times its dry weight in water dependent upon the charge of chemicals employed (Xiao & Meshitsuka, 2001). Jain et al. prepared superabsorbent hydrogels of wood cellulose fibers by grafting poly(methyl acrylate) onto softwood sulfite pulp fibers with ceric ammonium nitrate as the free radical initiator. Using this chemical grafting approach, they reported an improved water retention value of 91.2 g water/g pulp (Jain, Xiao & Ni, 2007). Cellulosic superabsorbents were also prepared by graft copolymerization of acrylamide (AM) onto wood pulp with a Ce^{4+} initiator, and N,N′-methylenebisacrylamide as the crosslinker. The obtained polyacrylamide (PAM)-grafted cellulosic copolymers

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Table 1
Fiber and fine lengths of softwood (SW) and hardwood (HW) kraft pulp.

	Fiber variety	Fluffed starting fiber	Wiley milled fiber through sieve size (mm)			Ball milled fiber
			3.00	1.00	0.50	
Fiber length[a] (mm)	SW	2.41	0.97	0.50	0.35	0.21
	HW	0.88	–	0.45	–	0.25

[a] Length weighted.

were alkaline-hydrolyzed to produce the water-absorbents. As PAM grafting yield increased, water absorbency properties shown to concommently increase also. With a PAM grafting yield of 210–240% the maximum water and saline absorbencies were reported to be around 2500 and 50 g/g, respectively (Kim & Mun, 2009).

Barcus and Bjorkquist developed a transesterification approach for crosslinking pulps using poly(vinyl methyl ether-co-maleic acid) (PVMEMA) and polyethylene glycol (PEG) which did not require a heavy metal as a catalyst for grafting. The thermally cured wood pulp-copolymer was then treated with a dilute sodium hydroxide solution and the resulting material could achieve water absorbencies of 15–100 g/g, dependent on reaction conditions (Barcus & Bjorkquist, 1991). Recently, Goetz et al. reported the preparation and characterization of a nanocomposite film from cellulose whiskers crosslinked with poly(methyl vinyl ether-co-maleic acid) and polyethylene glycol. The synthesized nanocomposites were reported to have a network structure and capable of absorbing up to ~900% water by weight of nanocomposite (Goetz, Mathew, Oksman, Gatenholm & Ragauskas, 2009).

Wood pulp based water superabsorbents have the potential of utilizing bleached kraft virgin or recycled fiber to form chemically crosslinked hydrogel materials. These cellulosic superabsorbents could be used in large volume applications, such as absorbents for hygiene products, agricultural packaging needs. In this paper, we have prepared crosslinked hydrogels based on wood pulp short fibers or fines by an esterification crosslinking reaction between bleached kraft fibers, PVMEMA and PEG. In addition, we have examined the effects of fiber length, curing time, the charge of PVMEMA on water absorbency properties.

2. Materials and methods

2.1. Materials

Bleached softwood kraft pulp used in this study was acquired from a southeastern U.S. kraft pulp mill bleached using a modern ECF bleach line. In addition, an ECF bleached birch kraft fiber was secured from a northern Scandinavia kraft pulp mill. Poly(vinyl methyl ether-co-maleic acid), with the trade name Gantrez S-97, from ISP Technologies, Inc., NJ, had an average molecular weight of 1.98×10^6 g/mol. Polyethylene glycol (PEG) with an average molecular weight of 3350 g/mol was purchased from Mallinckrodt Baker, Inc. The tea bags were made from tea bag paper which was cut into 4.7 cm × 9.5 cm rectangles and folded and sealed two sides with a pouch sealer. All other chemicals used in this study were purchased from VWR International and used as received.

2.2. Preparation of crosslinked water superabsorbent hydrogel

Dry SW and HW fiber boards were first manually disintegrated into ~3 cm × 3 cm pieces and then disintegrated using a Waring blender for 2 min to acquire a fluffy starting fiber. Short fiber samples were prepared by milling fiber board pieces with a Wiley mill equipped with 0.50–3.00 mm mesh sieves. The 0.50 mm Wiley milled fibers were further ball milled with a Retsch MM 200 mill for 60 min at RT with a weight ratio of fiber to balls of 1.00:5.60 to acquire cellulosic fines.

The size properties of the starting softwood and hardwood fibers, Wiley milled and ball milled fines were measured twofold using a Fiber Quality Analyzer (FQA) and these average results are summarized in Table 1. The refined short fibers were initially soaked in DI water and sonicated with an ultrasonic processor to release the agglomerated fines prior to FQA analysis (see Table 1). The FQA used in this study was set for fiber lengths from 0.07 to 10.00 mm, and the fine length was 0.07–0.10 mm (70–100 μm). The fine content for starting SW fiber was 2.23%; for the Wiley milled SW fiber samples, the fine contents were 2.31, 3.22, and 3.75% for the milled fibers through 3.00, 1.00, and 0.50 mm sieve, respectively. The fines content of the ball milled SW fiber was determined to be 7.24%. The fiber length of the Wiley milled and ball milled SW fibers were also characterized by scanning electron microscope, see Fig. 1. Although, it can be seen that Wiley milling shortened the fibers, did not generated more fines significantly. Ball milling further cut the fiber, made the fiber length dispersion slightly wider and yielded a minor increase in fibers that are shorter than 100 μm.

The reaction conditions employed for preparing cellulosic hydrogels are SW or HW cellulosic fiber or fines 3.00 g; PVMEMA 1.68, 2.51, 3.35, and 5.03 g; PEG 0.00 and 0.50 g; curing time 0.00, 4.00, 6.50, and 10.50 min; curing temperature 130 °C. The crosslinking reaction temperature was kept at 130 °C which according to Goetz, Mathew, et al. (2009) and Barcus and Bjorkquist (1991) was the preferred value for crosslinking.

Deionized (DI) water (30.00 mL) was adjusted to pH 2.88–2.98 with the addition of 0.50 N HCl solution, the PVMEMA was then added and the mixture was stirred at 65 °C ~1 h until polymer was fully dissolved. PEG was added to the PVMEMA solution and stirred for an additional 1 h. The resulting solution was cooled to RT and the cellulosic resource (3.00 g) was added and the mixture was stirred intermittently for 1 h. The slurry was then cast onto an aluminum foil and spread to form a ~1 mm thick pad and then dried at 65 °C until a constant weight was attained. The cellulosic pad was then cured at 130 °C for an assigned time.

2.3. Water absorption and retention value (WAARV) of produced hydrogel

The crosslinked cellulose test material (~6.80 g) was then manually disintegrated (~4 mm × 4 mm), suspended in DI water (500.00 mL) and stirred for 1 h. The pH of the cellulosic slurry was then adjusted to 2.00 and stirred in a Waring blender for 1 min. The cellulose suspension was filtered through VWR 415 filter paper and the residue was washed with DI water (500.00 mL) and then re-dispersed in DI water (500.00 mL). The pH of the suspension was adjusted to 8.50 using 0.50 N NaOH solution and kept at this pH for 24 h by occasionally adding NaOH solution. This procedure was performed in order to convert the free carboxylic groups (–COOH) of PVMEMA to carboxylate (–COONa) while retaining the crosslinked ester bonds. The fully swollen fiber slurry was collected by filtration through a Buchner funnel fitted with a paper handsheet forming wire (150 mesh) and washed with DI water. The weight and consistency of the slurry was measured and used to calculate the hydrogel yield and conversion (Barcus & Bjorkquist, 1991). An aliquot of the

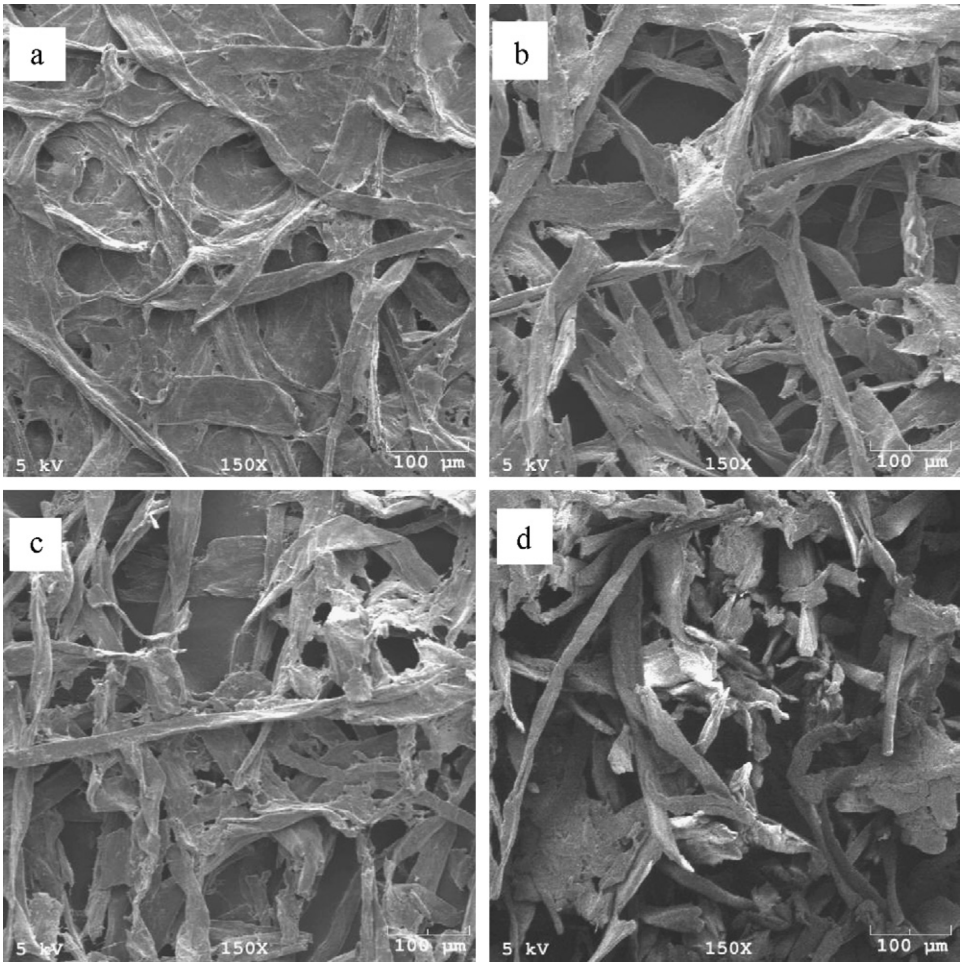

Fig. 1. SEM images of Wiley milled SW fibers: (a) 0.97 mm, (b) 0.50 mm, and (c) 0.35 mm and ball milled SW fibers: (d) 0.21 mm.

slurry was used for water absorption and retention value measurements. Additional aliquot samples of the slurry were used for SEM, FT-IR, and light microscopic analysis as described below.

An aliquot of the slurry (containing 0.25 g oven dried weight) was dispersed in DI water (175.00 mL). The stirred suspension was transferred into a pre-weighed tea bag and placed in a volumetric cylinder to allow the water to drain off. This sample (~0.1000 g oven dry wt) was placed in a centrifuge tube and centrifuged at 125 G for 10 min (Barcus & Bjorkquist, 1991; Cheng, Wang, McNeel & Jacobson, 2010; Dahou, Ghemati, Oudia & Aliouche, 2010). The centrifuged tea bag, with sample, was weighed to obtain the value of W_1 (see Eq. (1)). The sample was then dried in a 105 °C convective oven for 3 h followed by drying in a vacuum oven (60 °C) for 6 h and then cooled to RT in a desiccator. The dry mass of crosslinked cellulosics was weighed to get the value of W_2. Water absorption and retention values (WAARV, g/g) were determined by the following equation (Eq. (1)), and this WAARV measurement procedure was repeated 2–4 times and an average value of WAARV were acquired.

$$\mathrm{WAARV}\,(\mathrm{g/g}) = \frac{W_1 - W_2}{W_2} \qquad (1)$$

2.4. Light microscopic characterization of fibers or fines in hydrogel

An aliquot of the starting and crosslinked cellulosics (0.25 g o.d.) suspended in DI water (175.00 mL) were applied onto a microscope slide and then covered with a micro cover glass. A Leica DM IKM microscope operated with Simple PCI software was used to characterize the cellulosic materials.

2.5. FT-IR characterization of cellulosics

Samples (~2.50 mg) of dry bleached SW fiber, 130 °C cured SW fiber–PVMEMA, cured fiber–PEG–PVMEMA and NaOH neutralized (pH 8.5) and freeze dried cured SW fiber–PEG–PVMEMA were individually milled with KBr (0.50 g) in a mortar and pressed into FT-IR pellets. FT-IR spectra of these samples were collected on a Nicolet Magna-IR$^{\mathrm{TM}}$ 550 spectrometer in the 4000–400 cm^{-1} region with a spectral resolution of 4 cm^{-1} using 64 scans per spectrum in the absorption mode.

2.6. SEM characterization of cellulosics

An aliquot of starting and crosslinked cellulosics was lyophilized and then mounted on an aluminum stub and coated with Au–Pt alloy using an Anatech Hummer V sputter coater. The samples were imaged with a scanning electron microscope (Hitachi S-800) with 12 kV acceleration voltages.

3. Results and discussion

3.1. Effect of reaction conditions on WAARV

Fig. 2 illustrates the crosslinking chemistry between PVMEMA, PEG and cellulose as proposed by Barcus and Bjorkquist (1991) and

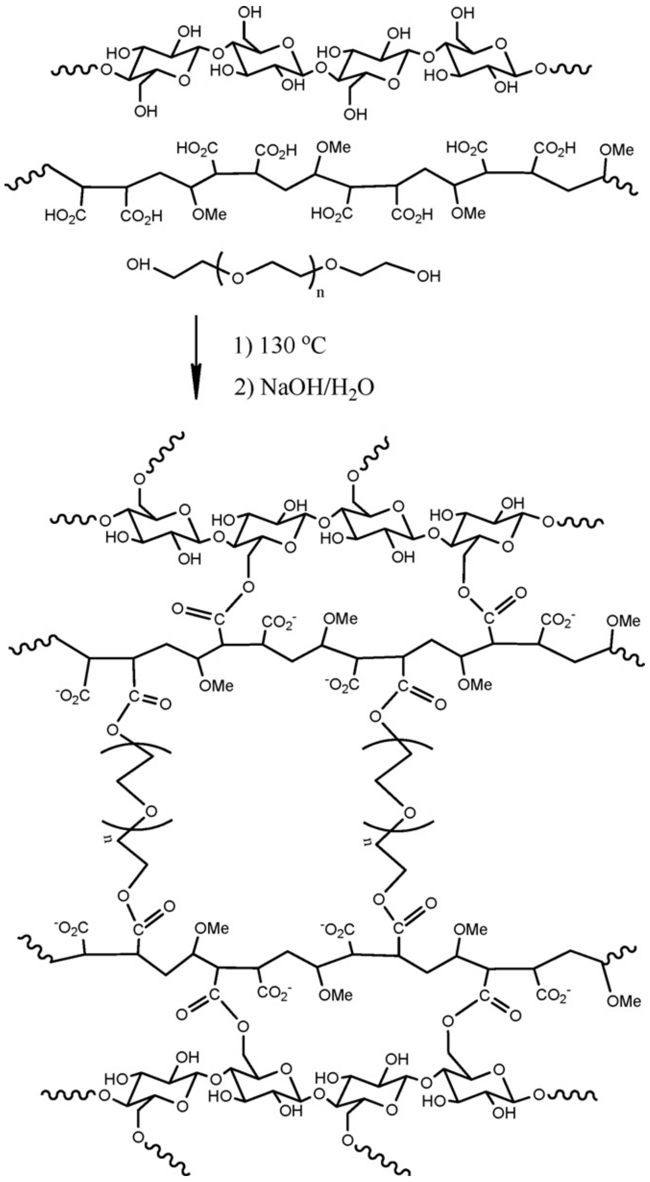

Fig. 2. Crosslinking reaction chemistry of mixture between PVMEMA, PEG and cellulosics and neutralization of the cured mixture to form water superabsorbent hydrogel.

Goetz, Mathew, et al. (2009). The transesterification reactions occur between the carboxylic acid groups of PVMEMA and the hydroxyl functional groups of cellulose and PEG yielding a cellulose polymer crosslinked material.

Following literature methodology (Barcus & Bjorkquist, 1991; Goetz, Mathew, et al., 2009), we examined the effect of softwood fiber length on the WAARV of crosslinked SW cellulosics which were prepared with a mass ratio of SW fiber:PVMEMA:PEG of 1.00:1.12:0.17 cured for 6.5 min at 130 °C (see Fig. 3A). It can be seen that the length of the softwood fiber employed impacted the water absorption and retention value of the synthesized hydrogels. The results indicate that for the conditions employed, optimal WAARV values were acquired with SW fibers milled to 0.50 mm. A further decrease in SW fiber length under the conditions employed resulted in a decrease WAARV. The WAARV values acquired on the crosslinked 2.41 mm SW kraft pulp fibers (i.e., unmilled) were comparable to literature values, while the WAARV of milled pulp fibers was much higher than reported values for traditional SW kraft pulps (Barcus & Bjorkquist, 1991; Jain et al., 2007).

Fig. 3B shows the effect of crosslinking reaction time on the water absorption and retention value (WAARV) of softwood (SW) short fiber-based hydrogels. It can be seen that for the conditions examined a crosslinking reaction time of about 6.5 min was optimal for an optimal WAARV value. Shorter reaction times presumably do not provide sufficient crosslinks while longer reaction times cause over crosslinking. Both are not beneficial for the synthesized hydrogels to absorb and retain water (Barcus & Bjorkquist, 1991). A curing time of 6.5 min was thus selected for all subsequent tests.

Fig. 4A compares the WAARV for milled and unrefined SW kraft fibers against the values for PVMEMA, PEG crosslinked cellulosic hydrogels synthesized from the corresponding cellulosics. It is clear that after crosslinking, the water absorption and retention ability of hydrogels increased dramatically by 1640–4850% compared to uncrosslinked fibers with the fiber lengths of 2.41, 0.97, and 0.50 mm, respectively. With a fiber length of 0.50 mm, the hydrogel WAARV (189.20 g/g) is 119% higher than that of the original fiber-based hydrogel (86.50 g/g). It also can be seen from Fig. 4A that the WAARV of the uncrosslinked SW fibers decreased as the length of SW fibers became shorter from 2.41 to 0.50 mm. This was attributed to the weaker capillary retention forces in the lumen of the milled fibers.

Fig. 4B presents the effect of PVMEMA charge on WAARV of hydrogels synthesized from 0.50 mm SW short fiber. It can be seen that as charge of PVMEMA was increased, the WAARV of formed SW short fiber-based hydrogel increased, this was tentatively attributed to an increase in the concentration of carboxyl groups. As the charge of PVMEMA was increased from 2.51 to 3.35 g/3.00 g cellulosics, the WAARV of synthesized hydrogels dramatically increased, then as the charge of PVMEMA increased further, the WAARV of hydrogels increased slowly. To balance the dosage of PVMEMA and the incremental increase of WAARV the mass ratio of charge of SW short fiber:PVMEMA:PEG of 1.00:1.12:0.17 seems best based on the reaction conditions employed.

In this work, PEG was used as the crosslinking agent between the PVMEMA units to yield the corresponding fiber–polymer hydrogel. While in this study, we have not attempted a detailed investigation of the effect of PEG charge on the hydrogel WAARV acquired from milled ECF bleached SW kraft pulps as this has been previously examined (Goetz, Sladky & Ragauskas, 2009, 2011). Preliminary results show that PEG plays a significant role in synthesizing the superabsorbent hydrogel which was cured at 130 °C for 6.5 min. Since if 0.50 g PEG was added with a mass ratio of SW fiber:PVMEMA:PEG of 1.00:1.12:0.17, the WAARV of the hydrogel was 189.20 g/g, much higher than the 4.80 g/g of WAARV of the hydrogel acquired in the absence of PEG with the same mass ratio of SW fiber:PVMEMA, and this WAARV was comparable to the starting pulp.

3.2. *Characterization of synthesized superabsorbent hydrogel by FT-IR*

Fig. 5 shows the FT-IR absorption spectra of 0.50 mm SW fiber (a), crosslinked 0.50 mm SW fiber–PVMEMA (b), cured 0.50 mm SW fiber–PEG–PVMEMA (c) and the freeze dried neutralized this crosslinked 0.50 mm SW fiber–PEG–PVMEMA network (hydrogel) with sodium hydroxide at pH 8.5 (d). The SW fiber spectrum (a) shows the absorptions of C–O–C ether linkage and hydroxyl group of the cellulose in the pulp fiber at 1170–1040 cm^{-1} and 3300 cm^{-1}, respectively (Ibrahim, 2002). The shoulder absorption around 2900 cm^{-1} was assigned to CH stretching vibrations. The absorption bands in the region 1200–1000 cm^{-1} are ascribed to the C–O stretching vibration of aliphatic primary and secondary alcohols in cellulose of the pulp fiber (Ibrahim & El-Zawawy, 2004).

Fig. 5b shows the IR absorption spectrum of cured 0.50 mm SW fiber–PVMEMA mixture. Apart from the absorption bands which

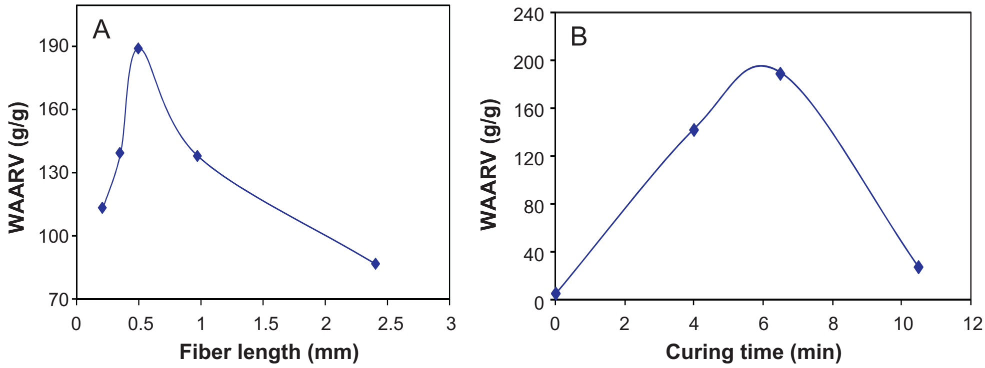

Fig. 3. Effect of fiber length and curing time on WAARV of hydrogels synthesized from SW kraft pulp fibers with a mass ratio of fiber:PVMEMA:PEG of 1.00:1.12:0.17, (A) cured at 130 °C for 6.5 min and (B) cured at 130 °C for various time intervals with 0.50 mm fiber.

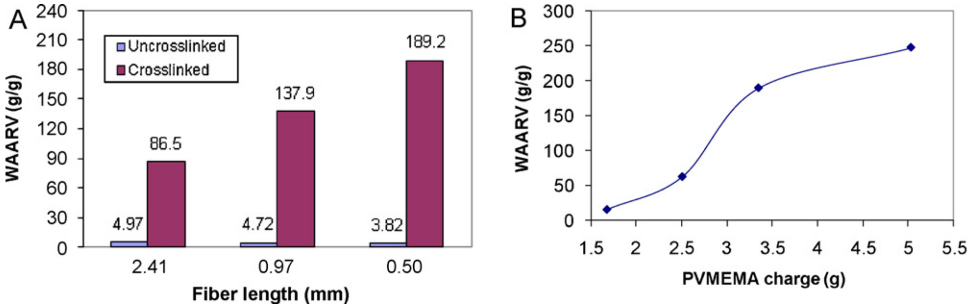

Fig. 4. Effect of crosslinking reaction on WAARV of hydrogels synthesized with a mass ratio of SW fiber:PVMEMA:PEG of 1.00:1.12:0.17 (A). Effect of PVMEMA charge on WAARV of hydrogels synthesized from 0.50 mm SW short fiber 3.00 g with PEG 0.50 g (B). The samples both in (a) and (b) were cured at 130 °C for 6.5 min.

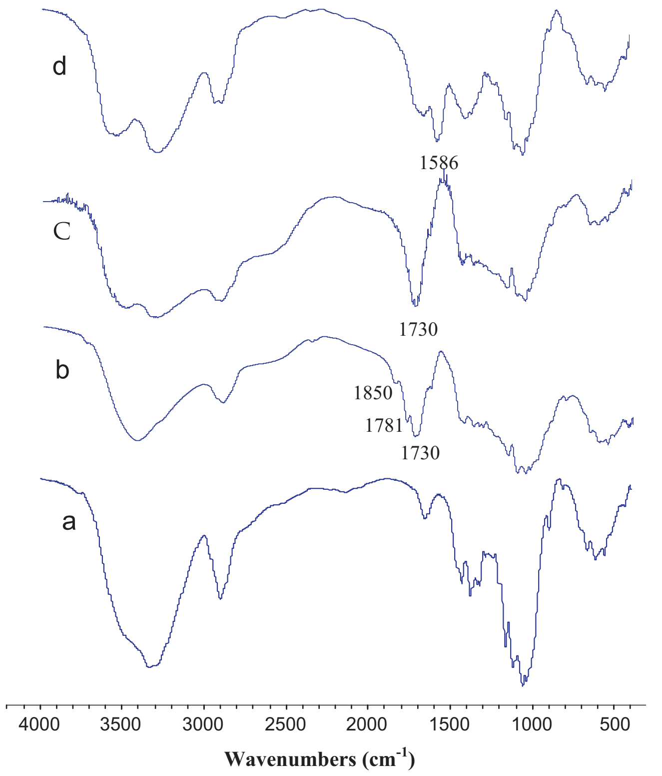

Fig. 5. FT-IR spectra: (a) bleached 0.50 mm SW fiber; (b) cured 0.50 mm SW fiber–PVMEMA (w/w of 1.00:1.12); (c) cured 0.50 mm SW fiber–PEG–PVMEMA (w/w of 1.00:0.17:1.12); and (d) NaOH neutralized (pH 8.50) and freeze dried cured 0.50 mm SW fiber–PEG–PVMEMA (w/w of 1.00:0.17:1.12). All samples were cured at 130 °C for 6.5 min.

appeared in cellulose in Fig. 5a, there are two new peaks at 1850 and 1781 cm^{-1} which were attributed to the asymmetric and symmetric stretching vibrations of a maleic anhydride formed during the curing process (Yang, 1993). The strong absorption peak at 1730 cm^{-1} results from the overlapping of the carboxyl carbonyl stretching band and ester carbonyl stretching band, the latter being formed by esterification between hydroxyl group of the short fiber and carboxyl group of the PVMEMA (Yang et al., 1996). The IR spectrum of cured 0.50 mm SW fiber–PEG–PVMEMA mixture is presented in Fig. 5c and it shows that the addition of PEG did not significantly change the characteristics of the IR spectrum compared to that of cured 0.50 mm SW fiber–PVMEMA mixture (b). The absorption of C–O–C ether linkages in PEG is overlapped with the absorption from cellulose of SW short fiber, while the two anhydride carbonyl bands at 1850 and 1781 cm^{-1} are no longer present. The possible ester carbonyl absorption formed by esterification between hydroxyl group of PEG and carboxyl group of PVMEMA coincides with the absorption of ester carbonyl formed by hydroxyl group of cellulose and carboxyl group of PVMEMA at 1730 cm^{-1}.

The alkaline treated cellulosic–PEG–PVMEMA hydrogel was washed, freeze dried and characterized by FT-IR as shown in Fig. 5d. From this data it can be seen that a new absorption peak at 1586 cm^{-1} appeared, which is attributed to the absorption of asymmetric stretching mode of the sodium carboxylate (Yang et al., 1996). The absorption of the stretching mode of carbonyl from ester remained at 1720–1730 cm^{-1}. The decrease in signal intensity is due to the carboxyl acid groups being converted to carboxylate leaving the ester bonds unreacted. The results of this FT-IR analysis support the overall crosslinking chemistry described in Fig. 2.

3.3. Characterization of synthesized superabsorbent hydrogel by light microscope

Fig. 6 shows the light micrographs of uncrosslinked SW fibers (A) and crosslinked SW fibers (B). The fiber lengths in both Fig. 6A

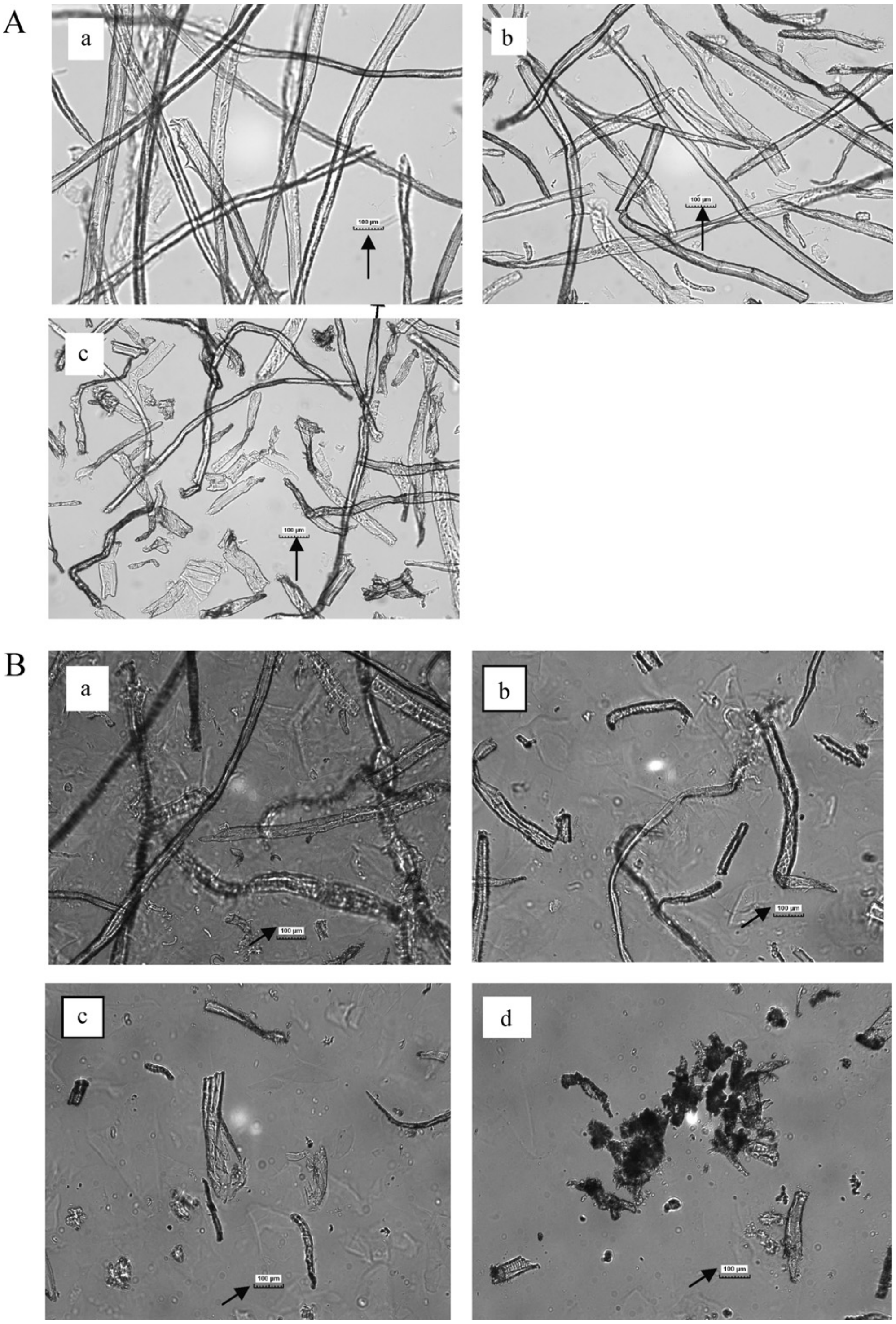

Fig. 6. Light micrographs of (A) uncrosslinked SW fibers and (B) crosslinked SW fibers in hydrogels. The fiber lengths in both (A) and (B) are a: 2.41 mm, b: 0.97 mm, c: 0.50 mm, and d: 0.21 mm, with a mass ratio of fiber:PVMEMA:PEG of 1.00:1.12:0.17, curing at 130 °C for 6.5 min (B). Scale bar is 100 µm indicated by arrow.

and B are a: 2.41 mm, b: 0.97 mm, c: 0.50 mm, and d: 0.21 mm. From the light microscopic images of the starting uncrosslinked fibers in water (Fig. 6A), it can be seen that the fibers or fines could be clearly imaged, and when performing the light microscopic analysis, the fibers or fines could move independently. Fig. 6B shows the light microscopic images of fibers or fines in the synthesized hydrogels at different resolutions. The fibers or fines did not move freely within the hydrogel for the samples were prepared and observed; moving as a whole instead. This was attributed to the crosslinking reactions which relatively fixed the fibers or fines within the hydrogels. Fig. 6B also shows that as fiber length was decreased from 2.41 to 0.50 mm (a–c), there were less uniformly dispersed fibers present in the hydrogel systems. While the fiber length was decreased further by ball milling, the shorter fibers tended to agglomerate together and these agglomerative fine clusters were not fully dispersed when hydrogel was prepared. Hence, the agglomerated crosslinked polymer–fiber network was not uniform and this was assumed not to be beneficial

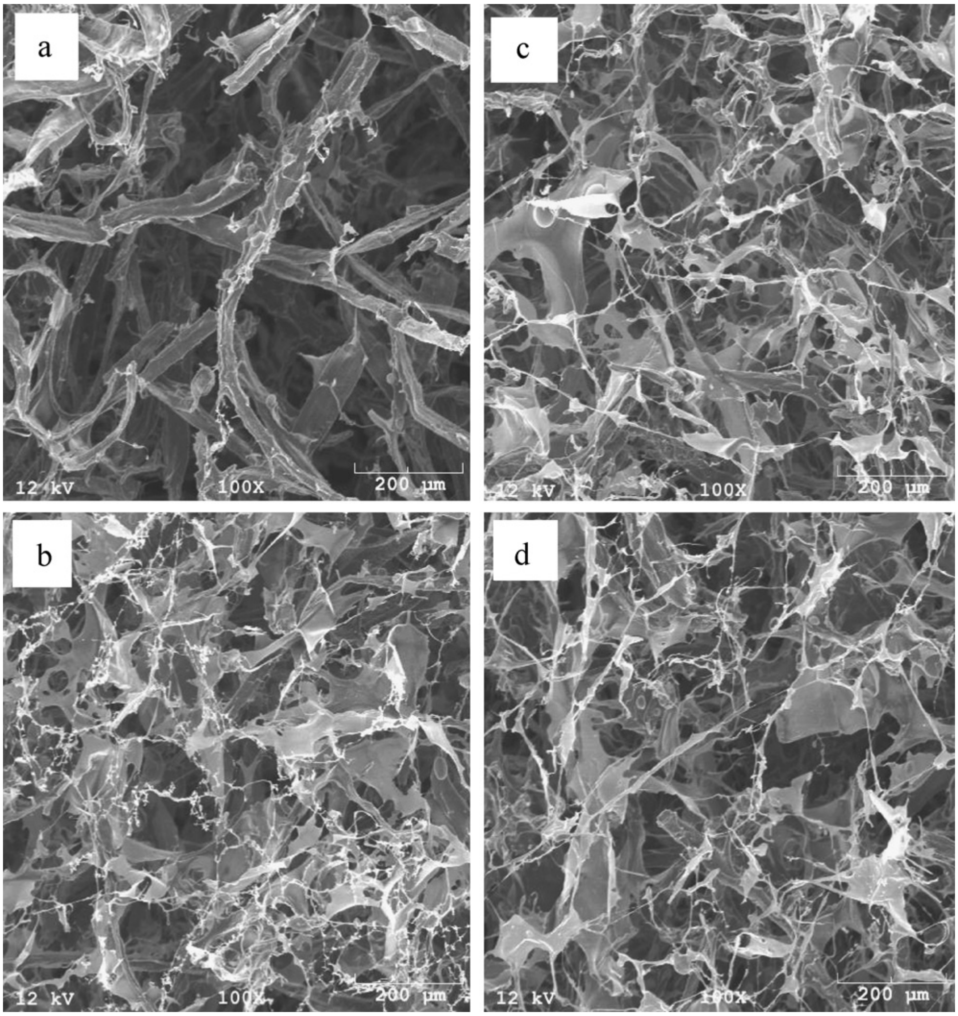

Fig. 7. SEM micrographs of freeze dried crosslinked and neutralized hydrogels, with a mass ratio of SW fiber:PVMEMA:PEG of 1.00:1.12:0.17, curing at 130 °C for 6.5 min, the fiber lengths: (a) 2.41 mm, (b) 0.97 mm, (c) 0.50 mm, and (d) 0.21 mm.

for water absorption and retention of the hydrogel (Fig. 6B-d).

3.4. Characterization of synthesized superabsorbent hydrogel by SEM

SEM characterizations of SW fiber-based hydrogel structures are presented in Fig. 7. It can be seen that the crosslinked SW fibers or fines present an open structure for the freeze dried crosslinked hydrogels. For the unrefined SW fiber-based hydrogels (fiber length is 2.41 mm), larger crosslinked pores were formed between fibers, and the SEM image suggests that the crosslinking polymer is present primarily on the fiber surface, and the polymers seemed not to form polymer bridges between fibers. While for other shorter fiber- or fine-based hydrogels (fiber lengths were 0.97, 0.50, and 0.21 mm, respectively), the crosslinking polymers appear to have formed bridges or networks between the short cellulosic fines.

Compared to unrefined SW fibers (fiber length is 2.41 mm), the refined fibers formed relatively smaller and denser tunnel structure. Among three refined SW short fibers, the 0.50 mm fibers seemed to form more uniform tunnel structure, and the polymers seemed to form more uniform networks. So based on these images, it could be reasonably inferred that 0.50 mm fibers could react with the hydrophilic polymers to form a crosslinking network structure whose pores were optimized to absorb and hold more water and water clusters. The 0.21 mm cellulosic fibers in hydrogel formed agglomerates or clusters which were attributed to the ball milling and these fines were not dispersed uniformly in the hydrogel structure (Fig. 6B-d) which may contribute to the reduced WAARV properties observed.

3.5. Preliminary testing of hardwood fiber-based hydrogel

In this study, a hardwood (HW) fiber-based hydrogel from birch was preliminarily examined using a mass ratio of HW fiber:PEG:PVMEMA of 1.00:0.17:1.12 and a curing time and temperature of 6.50 min and 130 °C, respectively. Fig. 8 presents the effect of fiber length on WAARV of HW birch fiber-based hydrogels (Fig. 8A). It shows that for the conditions examined, the hydrogel has the maximum WAARV value at a fiber length of 0.45 mm, which is comparable to that of the hydrogel synthesized from 0.50 mm SW short fiber. Fig. 8B shows the corresponding light micrographs of HW birch fibers with different lengths in hydrogels, it can be seen that when the fiber length is 0.45 mm, the fibers in the synthesized hydrogel dispersed more uniformly than did other two kind fibers which have the lengths of 0.88 and 0.25 mm. Fig. 8B also shows that by ball milling, 0.25 mm HW fiber formed agglomerative fine clusters, and these agglomerative fine clusters were not fully dispersed in synthesized hydrogel. This was assumed to account for

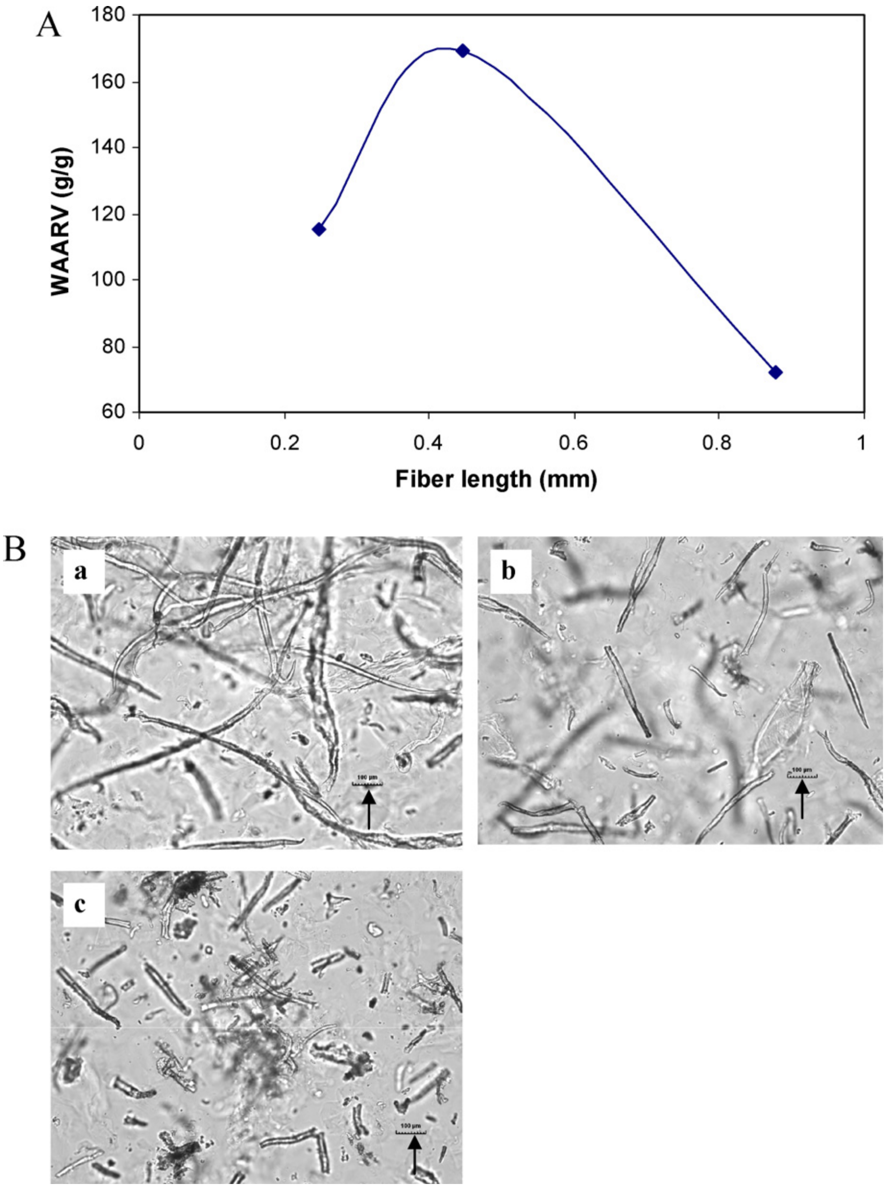

Fig. 8. Effect of HW birch fiber length on WAARV (A) and fiber dispersion (B) of hydrogels with the mass ratio of fiber:PVMEMA:PEG of 1.00:1.12:0.17 cured at 130 °C for 6.5 min. The fiber lengths are a: 0.88 mm, b: 0.45 mm, and c: 0.25 mm. Scale bar is 100 μm indicated by arrow.

that the hydrogel synthesized from 0.45 mm HW fibers achieved the optimal WAARV.

4. Conclusions

This paper presents a method to synthesize short wood cellulose fiber-based water superabsorbent hydrogels by grafting crosslinking reaction with poly(vinyl methyl ether-co-maleic acid) (PVMEMA) and polyethylene glycol (PEG). The effect of varying the fiber length of SW and HW kraft pulps on the WAARV of synthesized hydrogels was examined. For the conditions examined, an optimal crosslinking reaction time of 6.5 min at 130 °C was determined. For softwood (SW) fiber, when the fiber length is mechanically refined to a size of 0.50 mm, the synthesized hydrogel can absorb and retain 189.20 g water per gram of hydrogel, which is 119% higher than does the original fiber-based hydrogel. After curing, the water absorption and retention value (WAARV) of hydrogels increased dramatically by 1640, 2822, and 4853% compared to uncrosslinked SW fibers with fiber lengths of 2.41, 0.97 and 0.50 mm, respectively. Light microscopy and SEM analysis indicated that WAARV of hydrogels were affected by the kind of fiber employed (softwood or hardwood) and short fiber agglomeration and morphologies. These results indicate that the hardwood (HW) birch fiber-based hydrogels showed the similar relationship of fiber length and WAARV to that of SW fiber-based hydrogels.

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