

Preparation of Microwave-Assisted Polymer-Grafted Softwood Kraft Pulp Fibers. Enhanced Water Absorbency

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ABSTRACT: A wood pulp cellulose-based hydrogel material was prepared with poly(methyl vinyl ether-co-maleic acid) (PMVEMA), polyethylene glycol (PEG), and softwood ECF kraft pulp via microwave and thermal esterification and compared via hydrogel absorption and retention of water and 0.10M NaCl. The microwave initiated reaction time was optimized to 105 s at 1600 W based on maximum water absorption of 96 g/g of the 49% PMVEMA pulp hydrogels. The influence of reaction variables such as pulp fiber size and the weight ratios of PMVEMA to pulp were investigated. The maximum water absorbency of the milled pulp fibers microwave initiated products was 151 g/g, whereas the maximum water absorbency of the milled pulp fibers thermally initiated hydrogels was 198 g/g. In addition, the microwave initi-

ated hydrogels retained a maximum of 67% of absorbed water after centrifugation at 770 rpm for 10 min, whereas the thermally initiated hydrogels retained a maximum of 49% of water absorbed. Fourier transform infrared spectroscopy (FTIR) was used to confirm the esterification of the PMVEMA with the pulp cellulose. Microwave initiated crosslinking successfully produced a pulp hydrogel with a shorter reaction time and comparable or improved water absorption and retention properties when compared with the traditional thermally crosslinked pulp hydrogel system. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 387–395, 2011

Key words: hydrogels; biopolymers; crosslinking; fibers; renewable resources; swelling

INTRODUCTION

Currently, there is growing interest in developing new products from natural resources as sustainable alternatives to petroleum derived products. Cellulose is one of the key building blocks for creating sustainable biomaterials as a way to reduce the global carbon footprint and serve also as a key resource for biofuels.^{1–6}

The grafting of chemical reagents onto lignocellulose has been examined to determine the effects on the fibers. For example, the esterification of carboxylic acid containing polymers with wood pulps^{7–12} and cotton^{13–16} has demonstrated that this is a promising approach to enhance water absorption, increase wet strength, and to impart anti-wrinkle properties.

Common reaction methods of preparing esterified cellulose fiber based hydrogels have included free radical methods, such as ceric ion catalysts,^{17,18} sodium hypophosphite,^{19,20} and ATRP²¹ methods. However, esterification of cellulose with carboxylic acids using thermal curing methods has been successful without catalysts.^{10,12}

Although poly(methyl vinyl ether co maleic acid) (PMVEMA) has been used in oral gels under the trade name Gantrez S-97, there has been interest in expanding its use with cellulosic materials. Barcus and Bjorkquist developed a procedure for reacting PMVEMA and PEG with a variety of pulps using a thermally initiated dehydration reaction as an alternative method for grafting cellulose without the need for a metal catalyst.²² The treated pulps were shown to absorb water with a range of absorption of 25 g/g up to 90 g/g.

The use of microwave irradiation to induce multi-component polymerization reactions is a research topic of increasing interest.²³ The use of microwave irradiation to reduce reaction times is a well appreciated benefit in comparison to traditional thermal initiated reactions. For example, Satge et al. successfully esterified soluble microcrystalline cellulose with DMAP and lauroyl chloride using microwave

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irradiation with reduce reaction times ranging from 30 min to 2 days to 1 min.²⁴ Microwave irradiation of cellulose has been used to produce 6-amino-6-deoxycellulose,²⁵ esterification of cotton waste to produce cellulose laurate films,²⁶ transesterification of methyl esters of rapeseed oil with carboxymethyl-cellulose,²⁷ and graft polymerization of *N*-isopropyl acrylamide and methyl acrylate onto α -cellulose.²⁸

There has been interest in using microwave irradiation in the processing of pulps. For example, microwave irradiation of thermomechanical pulp was successful in increasing the brightness of the TMP by 20–25 points through bleaching with hydrogen peroxide and magnesium carbonate or calcium carbonate.²⁹

The use of microwave irradiation to facilitate the reaction of a wood pulp and carboxylic acid containing polymer, such as poly(methyl vinyl ether co maleic acid) (PMVEMA), has not been investigated. The aim of this work was to investigate whether microwave irradiation could be used to produce hydrophilic grafted softwood pulps at a reduced reaction time with water absorption properties comparable to that produced using thermal curing techniques.

MATERIALS AND METHODS

Materials

Poly(methyl vinyl ether-*co*-maleic acid) with an average molecular weight of 1.98×10^6 was provided by ISP Corp. NJ, under the trade name Gantrez S-97, in a dry powder form. Poly(ethylene glycol) with an average molecular weight of 3350 was supplied by VWR and used as received. All other reagents used were supplied by VWR and used as received. A commercial ECF bleached southern softwood kraft pulp (0.863 mm arithmetic average fiber length) was used as a source of cellulosic fibers. A sample of this pulp was mechanically milled using a Wiley mill to an average fiber length of 0.276 mm. Average fiber lengths were measured using a Fiber Quality AnalyzerTM, OpTest Equipment Inc., Canada.

Preparation of absorbent hydrogels

PMVEMA (3.35 g) and PEG (0.50 g) were added to D.I. water (40.00 mL), preheated to 68°C, and acidified to pH 2 with 1.00N HCl. ECF bleached softwood kraft pulp was then added with vigorous mixing yielding a viscous slurry.²² Three compositions were prepared and classified based on the percent PMVEMA used by mass and described based on the percentage of PMVEMA (i.e., 32%, 49%, and 66%). Table I further describes how the specific mass of pulp to PMVEMA and PEG were varied. This proce-

TABLE I
Reaction Mixtures of PMVEMA, PEG, and Pulp

PMVEMA (%)	PMVEMA (g)	PEG (g)	Pulp (g, OD)
32	1.67	0.50	3.00
49	3.35	0.50	3.00
66	6.75	0.50	3.00

cedure was repeated to prepare crosslinked hydrogel materials with a milled ECF bleached SW kraft pulp.

The slurry was spread (~ 3 mm) onto an aluminum foil, air dried, and then cured in either a microwave (Hobart, 1600 W) or thermal convection oven. The curing condition for the convection oven was 6.5 min at 130°C. The microwave curing conditions were optimized to an irradiation time of 105 s at 1600 W. The samples were then wetted in water (500.00 mL), dispersed using a blender for 60 s, and rinsed with water (1 l), and collected via suction filtration. The collected fibers were dispersed in water (500.00 mL) and the solution pH of this mixture was raised to pH 8.5 (1.00M NaOH, VWR), collected and freeze dried for further characterization.

Characterization

FTIR

FTIR spectra of the pulp, PMVEMA, PEG, and reaction products were obtained on a Nicolet Magna-IRTM 550 Spectrometer FTIR in transmission mode. Resolution for the infrared spectra was 4 cm^{-1} with 128 scans for each spectrum. The reacted crosslinked pulps were immersed in 0.10M NaOH solution for 5 min, air dried, ball milled for 1 min, and analyzed by FT-IR-DRIFTS.³⁰

Grafting ratio

Grafting ratio and efficiency was evaluated using Soxhlet extraction where 0.25 g of the crosslinked pulps were placed into a Whatman 603 cellulose thimble, washed with deionized water for 15 h, dried in a 105°C oven for at least 8 h, and weighed. The percentage of starting material remaining after the Soxhlet extraction was determined by the following equation,

$$\frac{SW_1 - SW_2}{SW_1} \times 100\%$$

Where SW_1 is the initial sample mass and SW_2 is the sample mass after Soxhlet extraction.

The estimated grafting ratio was determined using the following formulas,

$$\frac{SW_2 - P\% * SW_1}{PMP\% * SW_1} \times 100\%$$

Where $P\%$ is the theoretical percentage of pulp in the crosslinked pulp and $PMP\%$ is the theoretical percentage of PMA/PEG in the crosslinked pulp.

Water absorbency

Water and 0.10M NaCl sorption measurements of the crosslinked pulps and milled pulp were conducted using the traditional tea bag test method.³¹ Briefly, 0.10 g (oven dry g) sample (W_1) was added to a tea bag, heat sealed, weighed (W_2), and immersed in an aqueous solution for 8 h. The tea bag was subsequently allowed to drip dry for 10 min, weighed (W_3), and then centrifuged (770 rpm) for 10 min and reweighed (W_4). The tea bag was then dried in an oven and was reweighed for a final mass (W_5). The total water absorbed was calculated based on the following equation and is reported as g absorbed/ g dry hydrogel (g/g).

Absorption Value

$$\frac{W_3 - (W_1 + W_2)}{W_5 - W_2} \quad (1)$$

The retention value was calculated similarly and reported as g retained per g dry hydrogel (g/g). Replicates were measured and the average is reported with the error stated as the calculated standard deviation of all replicates.

Retention Value

$$\frac{W_4 - (W_1 + W_2)}{W_5 - W_2} \quad (2)$$

The percent retained is the average retention value divided by the average absorption value and multiplied by 100%. Student's *t*-test calculations were also conducted to assure statistical relevance.

Microscopy

SEM

Freeze dried crosslinked hydrogels were mounted on stubs and gold sputter coated prior to imaging. The fiber surfaces were studied with a LEO 1530 thermally-assisted field emission (TFE) SEM with a 10 kV acceleration voltage and a Hitachi S800 field emission gun SEM with a 15 and 20 kV acceleration voltage.

RESULTS AND DISCUSSION

Preparation of the superabsorbent hydrogels—determination of microwave settings and reaction time

The expected crosslinking reactions between the components, as shown in Figure 1, occurred when heated to 130°C. PMVEMA and the pine pulps are

expected to undergo an esterification reaction primarily between the primary hydroxyl group of the cellulose and the acid groups of the PMVEMA. The PEG should also react with the PMVEMA in a second esterification reaction. A prior communication demonstrated that all three components were necessary to achieve the maximum water absorption and retention capabilities. Goetz, L. A.; Sladky, J.; Ragauskas, A. J., *Holzforschung* 63, 414, 2009.

With the interest in utilizing microwave technology to induce this crosslinking (Fig. 1), the microwave power settings and irradiation times were optimized. The optimal microwave power settings and microwave irradiation times were determined by varying the power (1600 W, 800 W, and 320W) and length of microwave irradiation. 49PMVEMA-bleached kraft fibers were mixed into a slurry, spread thinly onto foil and removed after drying, and then microwave irradiated 45–105 s at 1600 W (high), 60–180 s at 800 W (medium), and 120–1200 s at 320 W (low) power. The final products were then evaluated based on the total water absorbed using the traditional tea bag test method. Figure 1 shows the chemical structures of PMVEMA, PEG, and the crosslinked hydrogel product. Figure 2 shows the trends for the 800 W and 1600 W reacted pulps.

After 105 s at 1600 W, the dried slurry started to char and longer reaction times exacerbated this and decreased the yield significantly. Similarly, the 320 W setting was not further evaluated when it was determined that after 600 and 1200 s, the water absorption was only 38.9 g/g and 45.3 g/g, respectively whereas the starting pulp had a value of 30 g/g. These water absorption values are less than the maximums achieved with the 1600 W setting while the irradiation time was greater than the reaction times used in the thermal curing process.

Figure 3 also shows the water retention capabilities of the 49PMVEMA-kraft pulp based hydrogels as microwave time and irradiation power level are varied. The water retention values change significantly based on microwave reaction time for the 1600 W power level pulps, while overall the 800 W power level microwaved hydrogels consistently decreased in the g/g water retained after centrifugation. Based on the water absorption and water retention results, the optimal curing conditions were 105 s microwave irradiation at 1600 W.

There was a similar trend with the percent water retention of the 49PMVEMA-kraft hydrogels as shown in Figure 4. When evaluated as the percentage of water retained based on the total amount absorbed, the 800 W irradiated pulps ranged between 29 and 32% water retained. The 1600 W irradiated hydrogels varied considerably more as time irradiated increased with the maximum water retained occurring with the 90 s irradiated pulp

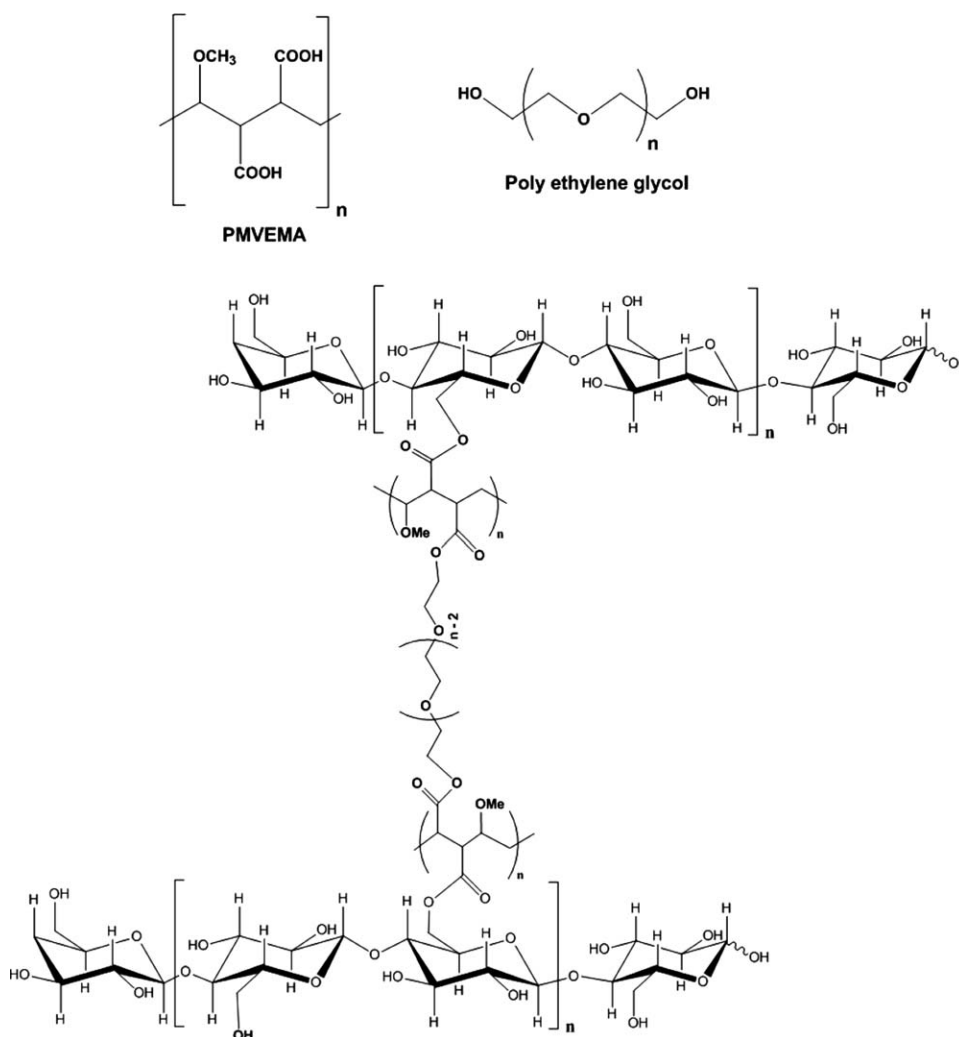


Figure 1 Chemical structures of PMVEMA, PEG, and expected crosslinked hydrogel product.

hydrogel (44%). These results show the influence that microwave irradiation time and power have on the reaction and formation of the PMVEMA-PEG-cellulose network.

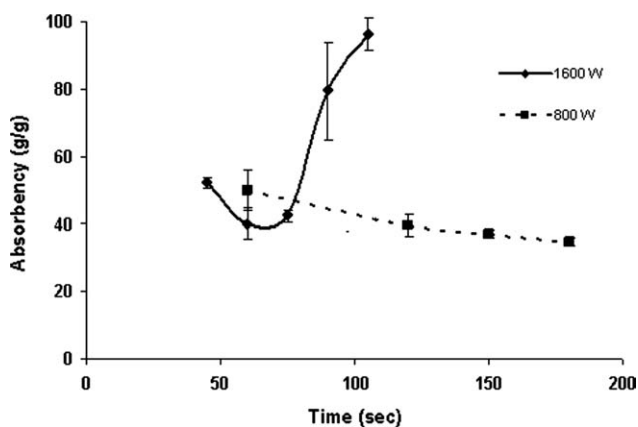


Figure 2 Effect of reaction time and power setting on water absorption of 49PMVEMA-softwood kraft pulp hydrogels.

Effect of PMVEMA on water absorption and retention

The influence that the PMVEMA had on water absorption and water retention of the PMVEMA-

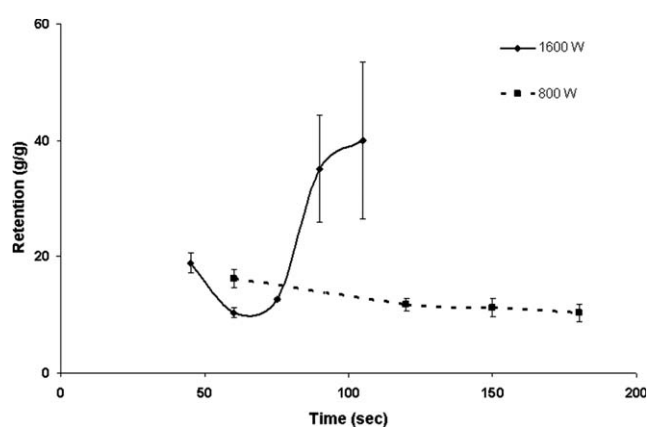


Figure 3 Effect of microwave irradiation time and power level on water retention of 49PMVEMA-softwood kraft pulp hydrogels.

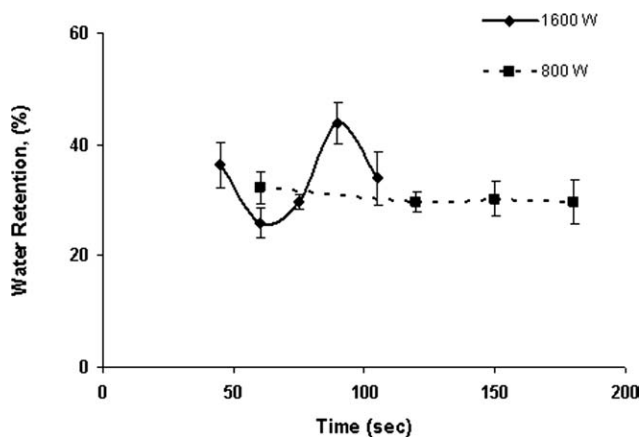


Figure 4 Percentage water retained by the prepared hydrogels as power and irradiation time is varied.

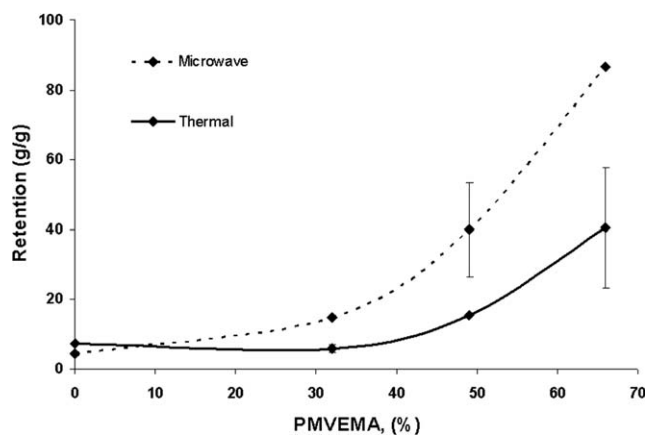


Figure 6 Water retention as PMVEMA is varied with microwave irradiated and thermal heated pine pulp.

PEG-pulp hydrogels was evaluated. The percent PMVEMA was varied in three different compositions of pine pulp based materials, 32%PMVEMA, 49%PMVEMA, and 66%PMVEMA. Figures 5 and 6 show the results of the water absorption and water retention as PMVEMA increased. The water absorption for all percentages is greater than the unreacted pulp. There is a significant difference between the water absorption capabilities of the pine pulp that is microwave irradiated versus the pine pulp that is thermally crosslinked. Most striking is the near three-fold increase in water absorption of the 49%PMVEMA-Microwave pulp when compared to the 49% PMVEMA Thermal pulp.

The water retention abilities of both the microwave and thermally treated pulps increase as PMVEMA is increased when evaluated as g water absorbed per g pulp (g/g) with Figure 6. However, when evaluated as a percentage of water retained (Figure 7), the microwave irradiated 66PMVEMA-kraft hydrogel retains 65% of the water absorbed while the thermally treated 66PMVEMA-kraft retains 44% of the water absorbed.

As controls, PMVEMA-PEG, pulp+PMVEMA, and pulp+PEG were prepared according to the established methods and characterized. Cured PMVEMA-PEG was shown to be soluble in water. The PEG treated pulps (pulp+PEG) absorbed and retained values similar to those of the unreacted pulp fibers. While the PMVEMA treated pulps did absorb more water than the untreated and PEG-treated pulps, they absorbed 21 – 259% less water than the PMVEMA-PEG pulps. These results highlight the need for having a three component mixture and in establishing the PEG’s involvement in enhancing water absorption which is attributed to its involvement in crosslinking chemistry as summarized in Figure 1.

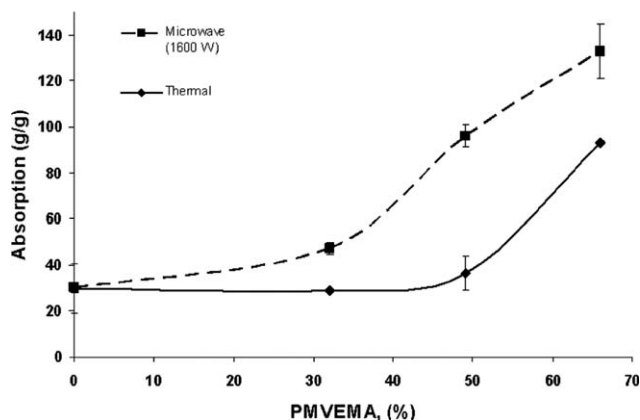


Figure 5 Water absorption as PMVEMA is varied with microwave and thermal reacted softwood kraft pulp.

Behavior of pulp hydrogels in 0.10M NaCl

The absorption and retention of the microwave irradiated hydrogels in 0.10M NaCl solution was determined using the same tea bag method and the centrifuge technique as for the water absorption/retention tests. Overall, the thermally cured pulp

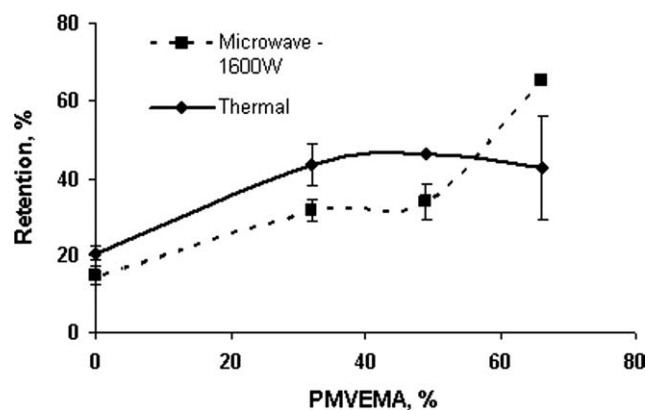


Figure 7 Comparison of percent water retained as PMVEMA is increased between microwave irradiated and thermally treated pulp hydrogels.

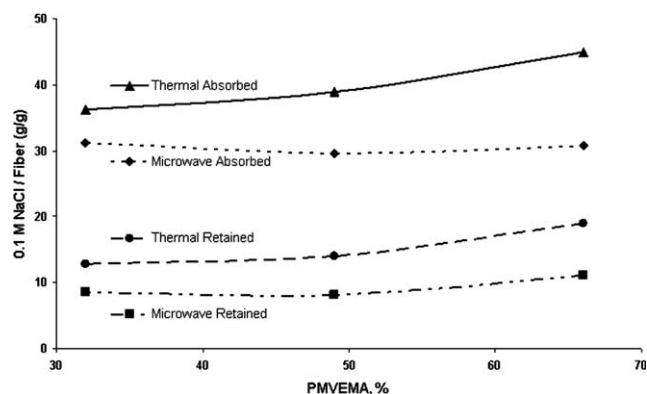


Figure 8 Absorption and retention of 0.1M NaCl solution by the microwave irradiated and thermally treated pulp hydrogels as PMVEMA is increased.

hydrogels absorbed and retained more 0.10 M NaCl solution than the microwave cured hydrogels. Both thermally cured and microwave cured hydrogels did absorb and retain more than the untreated pulp fibers in water (Fig. 8). Overall, there was little significant difference between the ability of the gels to absorb 0.10M NaCl solutions as the percent of PMVEMA increased, possibly indicating that a lower percentage of PMVEMA containing pulp may be effective enough in certain applications.

Effect of size of pulp fibers on water absorption and retention

The overall size effect of the pine pulp on water absorption was evaluated by milling the fully bleached kraft. The starting pulp had an arithmetic average fiber length of 0.863 mm (2.503 mm length weighted, 3.302 mm weight weighted) and after milling this was reduced to an arithmetic average value of 0.276 mm (0.455 mm length weighted, 0.652 mm weight weighted). The milled fibers were then reacted with the PMVEMA-PEG and cured under thermal and microwave irradiation conditions.

In general, the milled crosslinked pulps overall absorbed more water than the unmodified pulp hydrogels. For example, 68PMVEMA-Milled Thermal cured pulp absorbs ~ 100 g water/g fiber more than the 68PMVEMA-Thermal pulp, whereas the

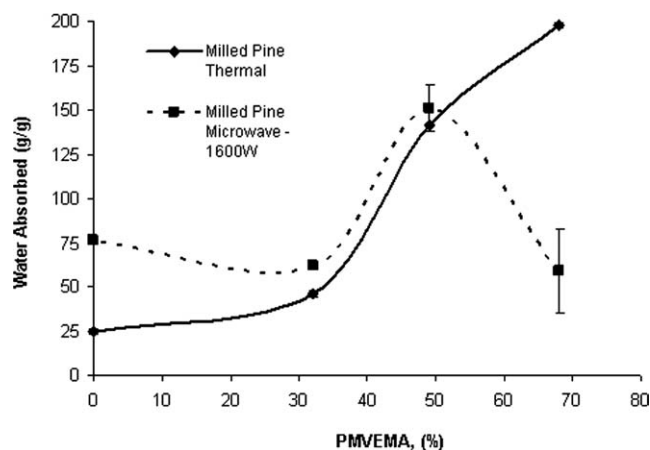


Figure 9 Water absorption of thermally cured and microwave irradiated milled pulp hydrogels.

49PMVEMA-Milled Microwave pulp absorbs 114 g/g water more than the 49PMVEMA-Microwave pulp. Figure 9 shows these trends. However, the 66PMVEMA-Milled microwave pulp does not follow this trend. This is most likely due to a greater degree of crosslinking occurring between the milled pine pulp and the PMVEMA.

The crosslinked hydrogels were Soxhlet extracted with water to compare the grafting efficiency of the hydrogels prepared with different starting pulp fibers size and crosslinking methods. The milled pulp fibers, both microwave and thermally cross-linked, had greater mass retention and grafting efficiencies (Tables II and III). The 32PMVEMA-Milled Thermal fibers had a 566% increase in grafting efficiency when compared to the 32PMVEMA - Thermal pulp fibers. Similarly, the 66PMVEMA-Milled Thermal fibers had a 154% increase in grafting efficiency when compared to the corresponding microwave pulp fibers. Overall, the milled pulp fibers demonstrate a greater grafting efficiency than the non-milled pulp fibers. This increase can explain the increase in water absorption of the milled pulp fibers. Microwave crosslinking of the milled pulp fibers resulted in grafting efficiencies similar to thermal crosslinking. However, microwave crosslinked pulp fibers at 32PMVEMA and 66PMVEMA resulted in grafting efficiencies that are 1.9 and 1.7 times

TABLE II
Percentage Retained of Starting Sample after Soxhlet Extraction

%PMVEMA	Pulp fibers		Milled pulp fibers	
	Thermal crosslinking (%)	Microwave crosslinking (%)	Thermal crosslinking (%)	Microwave crosslinking (%)
32	59.36	60.65	67.04	65.72
49	56.28	56.37	76.12	75.55
66	53.88	73.21	79.91	78.16

TABLE III
Grafting Efficiency of PMVEMA/PEG to the Pulp Fibers

%PMVEMA	Pulp fibers		Milled pulp fibers	
	Thermal crosslinking (%)	Microwave crosslinking (%)	Thermal crosslinking (%)	Microwave crosslinking (%)
32	3.228	6.317	21.51	18.37
49	29.04	22.098	57.36	56.34
66	35.04	62.27	71.71	69.24

greater than the respective thermally crosslinked pulp fibers.

FTIR spectroscopy

FTIR spectroscopy was used to evaluate the reactions occurring between the PMVEMA, PEG, and the pulps. Rocco et al. have investigated blends of varying percentages of polyethylene oxide (PEO) with a poly(methyl vinyl ether maleic acid) polymer using FT-IR and their methodology is applicable to our studies.³² Figure 10 illustrates the FTIR spectra of PMVEMA-PEG, PEG, and PMVEMA. The PEG spectrum (c) is a typical PEG FTIR spectrum with the expected C—O—C bands at 1151, 1109, and 1061 cm^{-1} .³² The PMVEMA spectra (b) shows the characteristic stretching bands between 1712 and 1743 cm^{-1} that are attributed to the carboxyl carbonyls from carboxylic acid groups of the maleic acid.¹⁵

In the PMVEMA-PEG spectra (a), both peaks attributed to the carboxyl carbonyl groups shifted to between 1728 and 1737 cm^{-1} , consistent with crosslinking occurring between the OH groups of the PEG and the COOH groups of the PMVEMA via esterification.¹⁵

Previous work has demonstrated that the esterification reaction between the PMVEMA-PEG and the pulps can be determined using FTIR.^{15,33} To separate the contribution of the esterified carboxylic acids

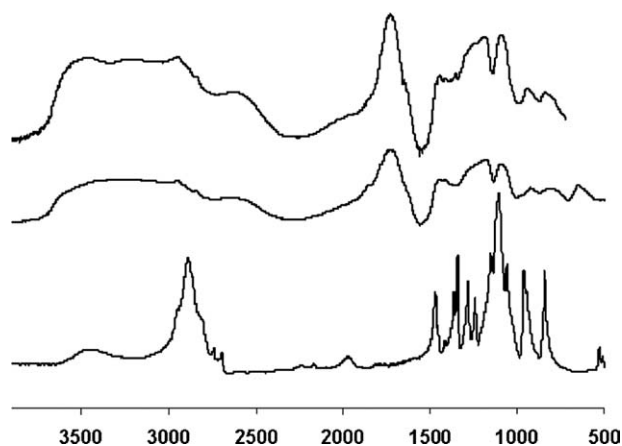


Figure 10 FTIR spectra of (a) PMVEMA-PEG, (b) PMVEMA, and (c) PEG.

with the unreacted carboxylic acids, the samples are briefly immersed in 0.10M NaOH to deprotonate the unreacted acid groups. This allows the bands now present in the carbonyl region to be able to be attributed solely to the esterified carboxyl groups. The carboxylated groups now appear in the FT-IR spectrum at 1588 cm^{-1} .

The FT-IR spectrum of the starting cellulose milled pine pulp shows the typical spectral bands associated with cellulose [Fig. 11(b)]. Specifically, the bands at 1112 cm^{-1} (asymmetric glucose ring stretch), 1163 cm^{-1} (C—O—C asymmetric vibration), 1061 cm^{-1} (C—O stretch), 1033 cm^{-1} (C—O stretch), and at 898 cm^{-1} (glucose ring stretch, C—H deformation). All of the modified pulp samples contain these absorptions. A control sample of PEG reacted with the milled pulp under the same conditions as the hydrogels were prepared resulted in a spectra that was unchanged from the unreacted milled pulp most likely because the PEG was washed from the system during the preparation. Figure 11(a) presents the FTIR spectrum of 66PMVEMA-PEG milled pine thermal hydrogel spectra treated with 0.10M NaOH.

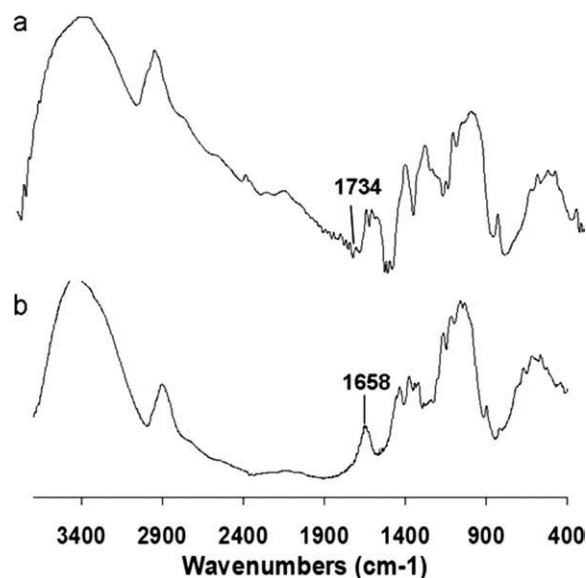


Figure 11 FTIR Spectra of Microwave Treated Pine Pulps (a) 66PMVEMA-PEG-milled pine pulp and (b) milled pine pulp.

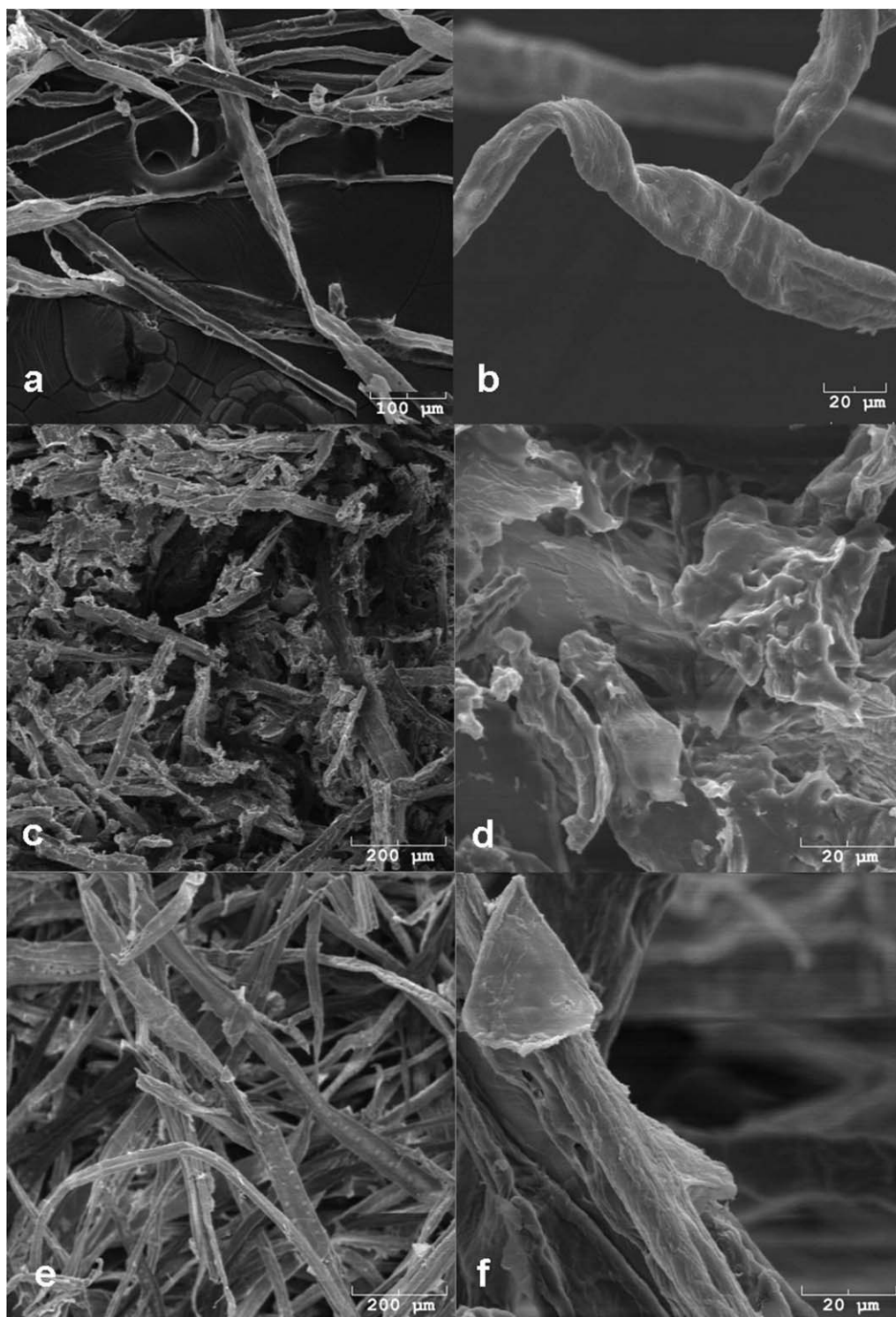


Figure 12 SEM images of (a) and (b) unreacted pine pulp fibers, (c) and (d) 66PMVEMA-Thermal, (e) and (f) 49PMVEMA-Microwave 120 s 800 W power.

The carboxylated band is evident at 1591 cm^{-1} as a result of immersion of the sample in the sodium hydroxide solution. This allows us to conclude that the bands at 1734 cm^{-1} are indicative of an esterification reaction between the PMVEMA and the cellulose.

SEM

The surface morphology of the fibers was investigated using scanning electron microscopy. As can be seen in Figure 12, the grafting on to the fibers for both curing techniques retains the fibrous structure of the starting pulp materials. As seen in Figure

12(a,b), the fibrils of the cellulose pulp are observed. When compared to Figure 12(c,d), the surface of the pulp displays none of these fibrils and instead appears to be relatively smooth. This suggests that the PMVEMA is reacting with hydroxyl groups on the surface of the pulp fibers. Figure 12(e,f) are examples of a microwave initiated crosslinked pulp hydrogel at 120 s, 800 W power (a suboptimal condition). Pulp fibrils are observed similar to those of the unreacted pulp potentially indicating noncomplete reaction between the PMVEMA-PEG and the cellulose where the nonreacted PMVEMA-PEG was washed away with water in the postreaction processing steps. This is further supported by the water absorption of these hydrogels (39 g/g) when compared to the hydrogels imaged in Figure 12(c,d) (93 g/g).

CONCLUSION

Microwave irradiation is an efficient method to produce PMVEMA-PEG crosslinked cellulose-based hydrogels, resulting in a reaction time of 105 s, significantly less than the reaction time of the thermally crosslinked procedure, 6.5 min. The thermal curing method is easily transferred to microwave irradiation as it does not utilize any heavy metal initiators. The microwave prepared hydrogels absorbed similar or greater amounts of water than the thermally prepared hydrogels. In addition, there appears to be a fiber size dependence to the water absorption abilities of this hydrogel for which the milled pulp based hydrogels absorbed 30–292% more water than the non-milled pulp hydrogels (with the exception of the 66PMVEMA-PEG Milled Microwave which absorbed 56% less water), explained by corresponding increase in the grafting efficiencies of the milled pulps. SEM analysis demonstrated that the PMVEMA-PEG matrix in both the microwave initiated and thermal crosslinking procedures appeared to stay on the fiber surface and resulted in similar surface morphology.

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