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Crosslinked hemicellulose citrate–chitosan aerogel foams

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ABSTRACT

The applications for hemicellulose are currently very narrow, because of its low molecular weight and varying chemical composition. In this research, novel applications for modified hemicellulose are developed making it a valuable biomaterial for absorbency applications in health care and medical textiles. The incorporation of carboxylic acid groups into hemicellulose via reaction with citric acid followed by cross linking with chitosan greatly improve the properties relative to hemicellulose, chitosan, a cellulose sponge product, and hemicellulose citrate alone. Optimum conditions for the cross linking of the hemicellulose citrate–chitosan include a 2.5 h reaction time at 110 °C with pH 3.5, a solid to liquid ratio of 1:100 and a hemicellulose citrate to chitosan ratio of 1:1 (w/w). The hemicellulose citrate–chitosan crosslinked foam is elastic, very soft, highly porous and durable. The hemicellulose citrate–chitosan can absorb up to 100 g of a saline solution per gram of material and up to 80 g of water per gram of material. Analysis of the hemicellulose citrate–chitosan foams with FTIR, DMA, and SEM confirms the crosslinked and hygroscopic behavior of the materials.

1. Introduction

The health care and medical textile industries may benefit from the utilization of biomaterials with performance properties comparable to petroleum based synthetic materials. These benefits may include a more stable raw material supply and cost, improved biocompatibility, and the use of renewable resources. Hemicelluloses represent about 20–35% of lignocellulosic biomass in trees and plants. Hemicelluloses are estimated to account for one-third of all renewable organic carbon available on earth (Prade, 1995; Sjöström, 1981). Often, hemicelluloses are found as organic wastes or byproducts of renewable forest and agricultural products (Badal, 2003; Ebringerova & Hromadkova, 1999). Unlike cellulose, hemicelluloses have not yet found broad industrial applications (Sun, Sun, & Sun, 2004), because of low molecular weight, branching and varying chemical composition.

In the pulp and papermaking process, significant quantities of hemicellulose are dissolved and burned as fuel. Worldwide, approximately 400 million tons of paper products are produced per year from approximately 600 million tons of wood. The majority of hemicellulose material associated with this wood is burned and a smaller fraction is retained in the paper product. The portion of hemicellulose that is burned can be roughly estimated at about 40 million tons per year. The development of new, high-valued co-products based on hemicelluloses would significantly improve the economics of lignocellulosic biomass to ethanol, paper, wood or other material processes.

Hemicelluloses are branched polymers of low molecular weight with a degree of polymerization in the range of 80–200 (Sjöström, 1981). The most common sugars found in hemicelluloses are D-glucose, D-mannose, D-xylose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid (Gabrielii & Gatenholm, 1998). Chemical composition and structure vary with plant species. The chemical modification of hemicelluloses presents a means for preparing materials with unique properties that can increase value and utility of these biopolymers. Modifications or applications that can accommodate or overcome issues with molecular weight dispersity or variations in chemical composition are required.

The incorporation of carboxylic acid groups in hemicellulose can improve the chemical and physical functionality of these materials. Natural polysaccharides with high carboxylic acid content are expected to have superior hydrophilic properties useful in absorbent applications. Salam, Pawlak, Venditti, and El-Tahlawy (in press, 2010) have determined that starch citrate and hemicellulose citrate had significantly increased water affinity relative to starch and hemicellulose (Salam et al., in press), producing a water soluble polymer. Further, a hydrophilic aerogel was formed when the starch citrate was blended and reacted with chitosan and freeze dried (Salam et al., 2010). Chitosan is another carbohydrate based polymer that is abundant as a byproduct of the seafood industry, is widely available and of strong research interest (Helander, Nurmiaho-Lassila, Ahvenainen, Rhoades, & Roller, 2001). Certain

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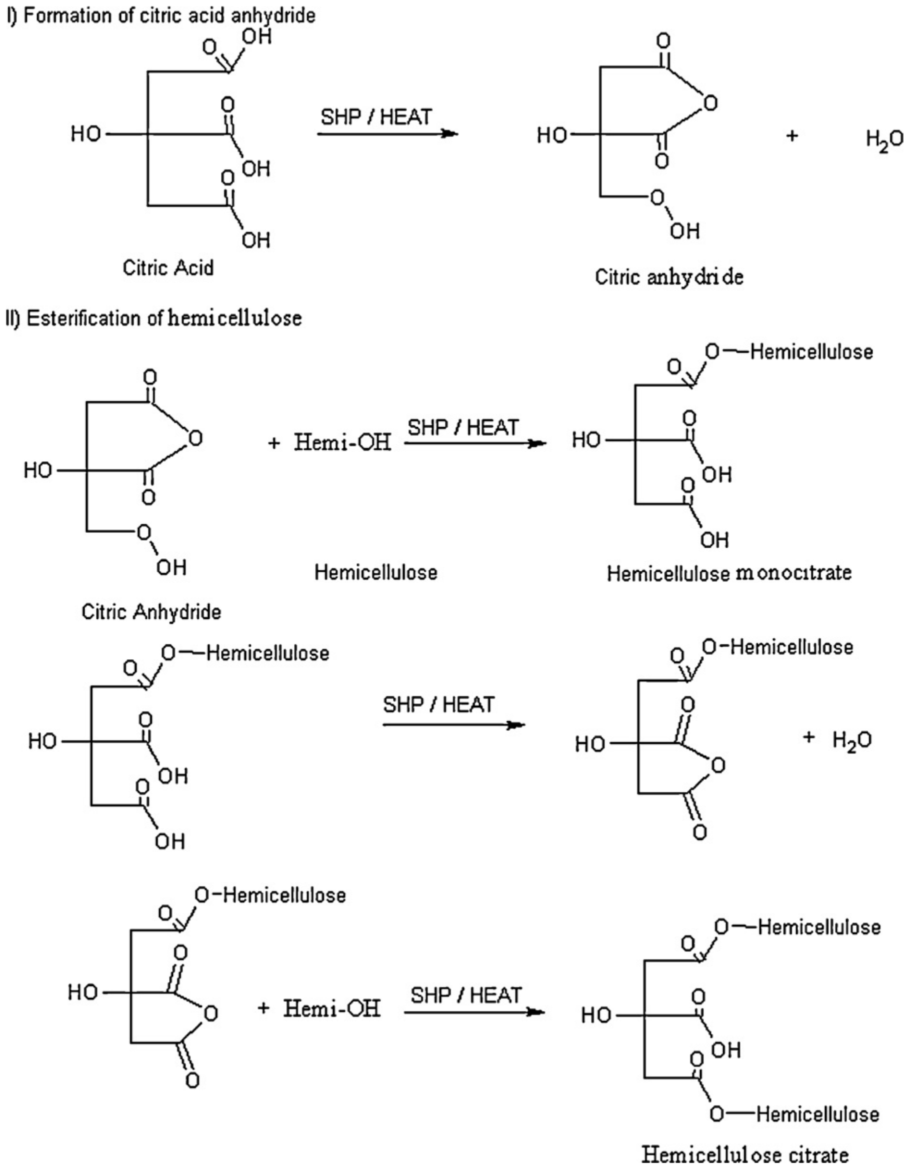

Fig. 1. Esterification of hemicellulose with citric acid.

forms of chitosan have been reported to have anti-microbial properties (Helander et al., 2001; Muzzarelli et al., 1990; Zheng, Zhu, & Sun, 2000). An extensive review of chitosan's pharmalogical characteristics can be found in the review of Kumar, Muzzarelli, Muzzarelli, Sashiwa, and Domb (2004). The starch citrate–chitosan aerogels had superior water and saline absorption properties relative to starch citrate and similar saline absorption as a commercial super absorbent based on acrylic acid (Salam et al., 2010).

The present investigation reports on the synthesis and characterization of a hemicellulose citrate–chitosan gel as an absorbent foam material. The effect of cross linking reaction conditions on the water absorbency, weight loss in water, and strength of the crosslinked product are discussed.

2. Materials and methods

2.1. Materials

The hemicellulose (HC) utilized was xylan from birchwood (poly ß-D-xylopyranose [1 → 4]) with xylose residues of greater than 90% by high performance anion-exchange chromatography (HPAE) purchased from Sigma–Aldrich, St Louis, MO (product number X0502). For calculation purposes the molecular formula used was $(C_5H_8O_4)_n$ with an average hydroxyl content per sugar moiety equal to one. The chitosan (medium molecular weight, degree of deacetylation 75–85%) CAS registry number 9012-76-4 was purchased from Sigma–Aldrich, St Louis, MO. The following reagent grade chemicals were also used: sodium hypo-phosphite (SHP) CAS registry number 123333-67-5, citric acid (CA) CAS registry number 77-92-9, sodium chloride, acetic acid, and sodium acetate from Fisher Scientific, Fair Lawn, New Jersey. Whatman filter paper (quantitative number 4, 110 mm diameter) from Whatman International Ltd., Maidstone, England and deionized water was used throughout. A superabsorbent material (particle size 0.8–1 mm, Small Polymer) based on poly acrylic acid (Watersorb, Fayetteville, Arkansas) and a commercial cellulose foam with tradename Spontex (Mapa Spontex Inc., Columbia, TN) were also used as controls. The sponge manufacturer reports the sponge composition to be 48% pulp, 28% magnesium chloride and 24% cellulose fiber.

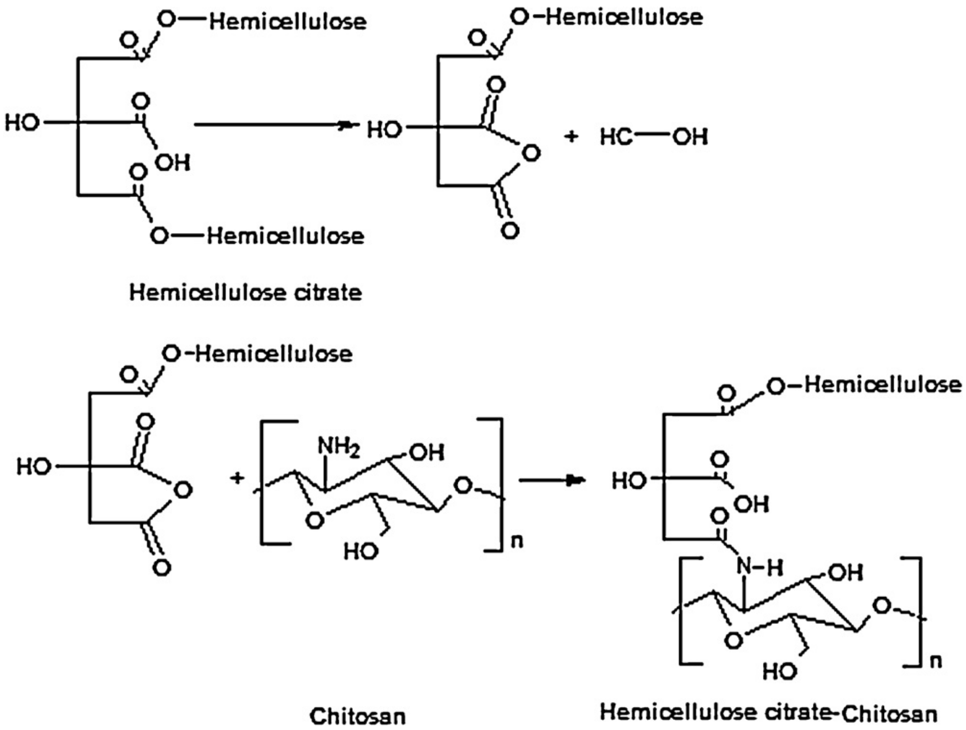

Fig. 2. Cross linking of hemicellulose citrate with chitosan. Note that the cross linking reaction does not require that citric acid first crosslinks the hemicellulose. It is possible for a similar reaction to occur if citric acid is only bonded to a single hemicellulose molecule.

2.2. Synthesis of hemicellulose derivative with citric acid in semi-dry oven

The esterification of hemicelluloses with citric acid reaction scheme is shown in Fig. 1. Citric acid (5 g) and sodium hypophosphite (1 g) were dissolved in a minimal amount of water (6 ml) in a beaker. Hemicellulose (5 g air dried) was combined with the citric acid solution in a 100 ml glass beaker and mixed vigorously with a glass rod. The mixture was placed in a forced air oven to dehydrate at 100 °C for 30 min. At this point, all surface moisture was removed and the hemicellulose particles were coated with citric acid. The oven temperature was increased to 115 °C (ramp took about 5 min) and the material was allowed to react for 5 h. The times and temperatures for reaction were determined from several previous trial

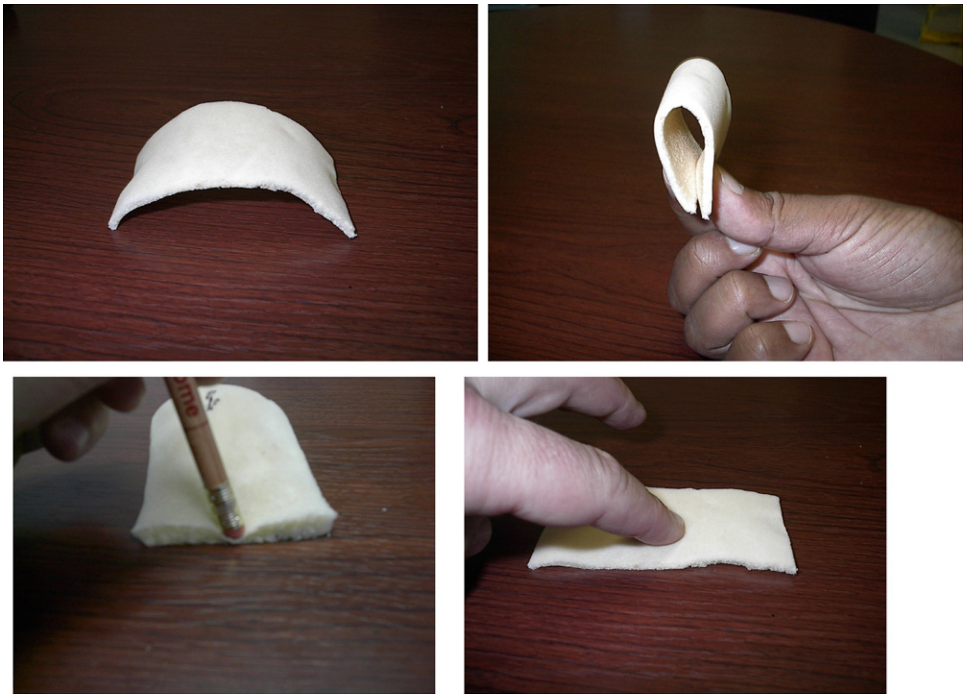

Fig. 3. Flexible foam material from hemicellulose citrate chitosan. From top left clockwise: unstressed foam, folded foam, localized impression, and flattened foam. After each of these deformations the unstressed shape of the foam returns. Reaction conditions: 1:1 of HC:C, 3 h, solid to liquid ratio 1:100, pH 3.5, 110 °C (optimum).

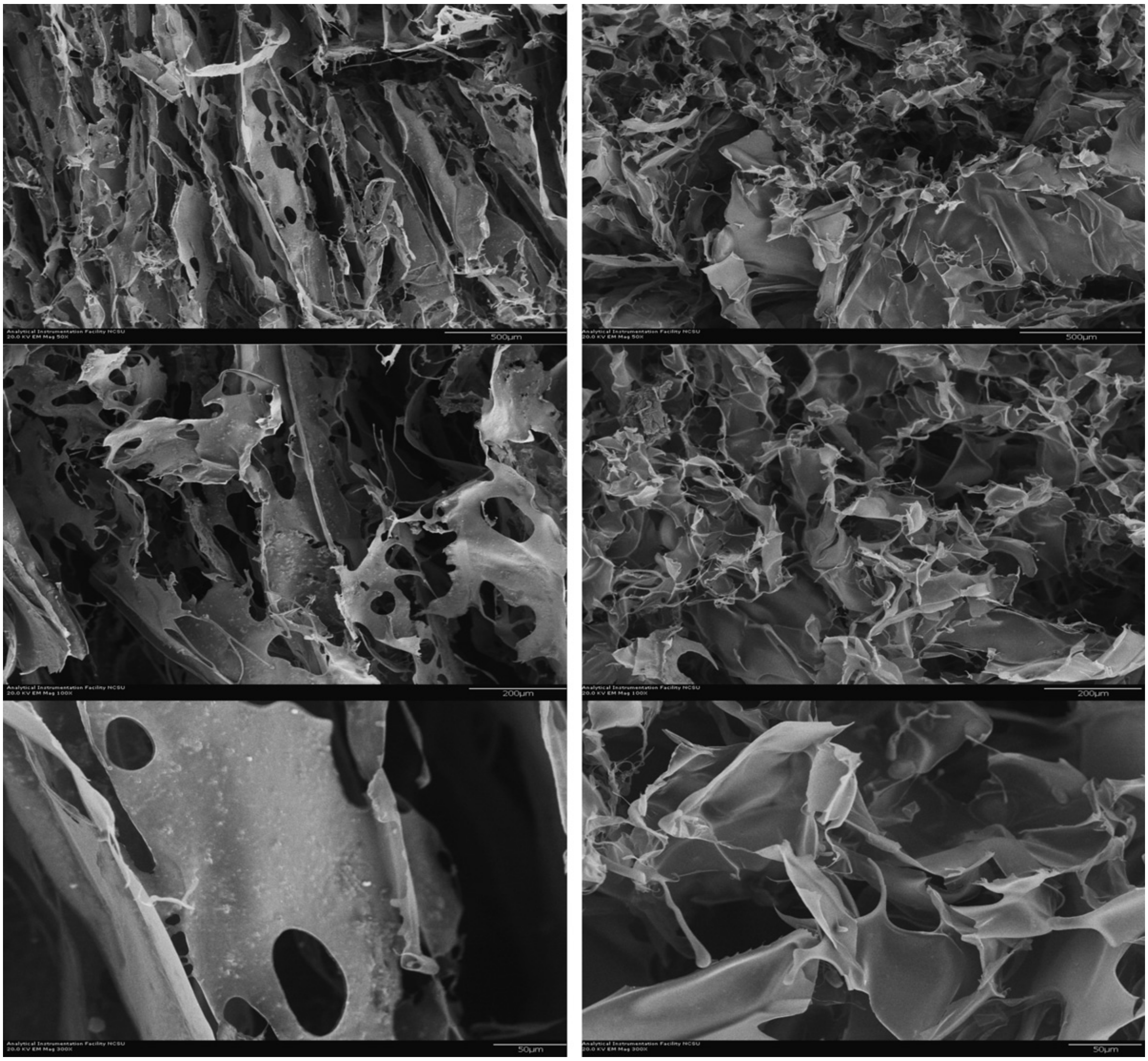

Fig. 4. Hemicellulose–chitosan foam (left) and hemicellulose citrate–chitosan foam (right). Top to bottom images have length scales of 500, 200 and 50 µm.

experiments in which times and temperatures were varied. Reaction products were slurried in water (60 ml) for 30 min, adjusted to pH 2 using acetic acid, filtered on filter paper, and washed with water (100 ml). The hemicellulose citrate (HC) product was air dried overnight, and the material weighed to determine yield (Demitri et al., 2008).

2.3. *Cross linking reaction*

A schematic of the cross linking of hemicellulose citrate with chitosan is shown in Fig. 2. A chitosan solution was prepared by adding 1 g of chitosan to a mixture of 99 ml of water and 1 ml of glacial acetic acid. The chitosan solution was added to 100 ml of a 1% hemicellulose citrate solution in a 500 ml round bottom flask. The pH was then adjusted to 3.5 with sodium acetate. The reaction mixture was stirred using a magnetic stirrer with the flask placed in an oil bath at 110 °C for 3 h. Water evaporation was controlled by the use of a condenser. Following the reaction, the reaction mixture was cooled to room temperature (approximately 1 h) and the hemicellulose citrate–chitosan aerogel product was then formed by freeze drying.

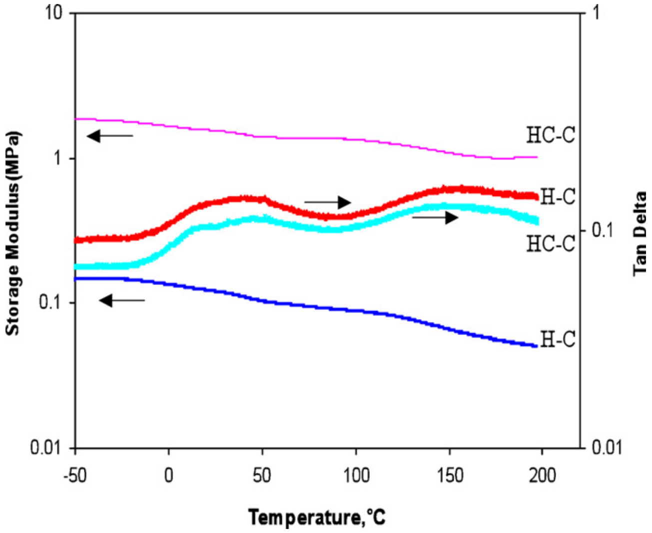

Fig. 5. DMA of (H–C) hemicellulose–chitosan and (HC–C) hemicellulose citrate–chitosan foam. Reaction conditions: 1:1 of HC:C, 3 h, solid to liquid ratio 1:100, pH 3.5, 110 °C.

2.4. *Measurement of absorbency and weight loss*

The section below describes three different techniques for measuring the water absorption and weight loss of absorbent materials. All techniques were found to be reproducible to within 10% of the measured values.

2.4.1. *Decantation method*

A decantation method was used to determine the water absorption of samples. The sample of about 0.1 g was weighed (to 0.1 mg), placed in a glass Petri dish of known weight and soaked in 50 ml of distilled water for 1 h. The water was carefully removed manually with a 25 ml pipette. The dish and sample were weighed and placed in an oven at 105 °C for 2 h. After cooling in a desiccator, the dish and sample were weighed to determine water absorption and weight loss. Absorption and weight loss with an aqueous NaCl solution (concentration: 0.9%) was investigated similarly (Gabrielii & Gatenholm, 1998). For some samples, the dimensions of the swollen samples were measured using a digital slide caliper. Foams evaluated were rectangular in shape. The superabsorbent material was spherical when dry and disk shaped when wet.

2.4.2. *Equilibrium swelling (ES) method*

The equilibrium swelling was determined by a gravimetric method. The sample was immersed into water in a Petri dish at room temperature for a predetermined time (1 h), and then poured into a pre-weighed wet tea bag (200 mm × 100 mm). The excess water was allowed to drip off the sample due to gravity. The wet weight of the tea bag and sample was then measured (X_a), and the equilibrium swelling (ES) was calculated according to the following formula:

$$\mathrm{ES} = \frac{X_a - Y_b - Z_p}{Z_p}$$

where Y_b is the weight of wet tea-bag and Z_p is the weight of dry sample.

Absorption and weight loss with an aqueous NaCl solution (concentration: 0.9%) was investigated similarly.

2.4.3. *Vacuum filtration method*

Approximately 0.1 g of each sample was weighed and placed in a glass Petri dish. The sample was soaked in 50 ml distilled water for a predetermined time (1 h). A dry Whatman #4 quantitative filter paper circle was placed into a Buchner funnel attached to house vacuum. The contents of the dish were poured onto the filter paper. The dish was rinsed with about 15 ml of additional DI water and this water was also poured into the funnel. Once the water was removed, the sample was lifted off the filter paper and then weighed to determine water absorption per gram of sample. Absorption and weight loss with an aqueous NaCl solution (concentration: 0.9%) was investigated similarly.

2.4.4. *Liquid absorption under load*

Pre-weighed samples (0.05 g) were equilibrated in saline solutions (0.9% NaCl by weight) for 1 h. The material was then removed from the solution and placed in the middle of six research grade blotter paper sheets and a weight of 6810 g applied over an area of 19.6 cm^2 for 20 min. This equates to a pressure of 0.337 kPa gauge (4.90 psig). Some of the water is transferred to the blotter paper during the pressing. The sample was then removed from the blotter paper and weighed. The saline solution absorbed after pressing/sample weight (% w/w) was calculated.

2.5. *Characterization*

FTIR spectra were recorded on a NEXUS 670 FTIR spectrophotometer using a KBr disc containing 10% finely ground samples. All the spectra were obtained by the accumulation of 256 scans, with resolution of 4 cm^{-1}, at 400–4000 cm^{-1} (Demitri et al., 2008).

Morphological characterization of starch citrate–chitosan microcellular foams was performed on images acquired using a scanning electron microscope (SEM), Hitachi S-3200N. The samples were fractured after freezing in a liquid nitrogen bath and then coated with platinum of 10 nm thickness to make the samples conductive (El-Tahlawy, Venditti, & Pawlak, 2007).

The hemicellulose citrate–chitosan foam was equilibrated in a conditioning room with an atmosphere of 23 °C and 50% relative humidity air for 48 h. The sample size was approximately 30 mm × 10 mm × 4.1 mm. The tensile strength of the hemicellulose citrate–chitosan foam was measured using an Instron 4411 (Canton, MA) tensile testing machine in the same conditioning room. The crosshead speed was 2 mm/s.

Dynamic mechanical analysis was performed with a DMA Model 2980 (TA Inc., New Castle, DE, USA) in the film-tension mode. Sample dimensions were approximately 30 mm length, 10 mm width and a 3.5 mm thickness. Samples were heated from −50 to 200 °C at 2 °C/min (static strain of 0.67%, 20 μm amplitude, 1 Hz). Each sample was measured for length, width and thickness before mounting (Walker, 2001).

The void fraction of the hemicellulose citrate–chitosan foams was calculated as one minus the foam density divided by the wall density. The total volume of a pre-weighed foam sample was determined by placing the foam in a cylinder with known volume and then adding small beads (average diameter of 2.5 mm) to fill the volume. The beads total mass and packing density was also known. By subtracting the volume of the beads, the foam volume is ascertained.

The hemicellulose citrate–chitosan cell wall material density was estimated by preparing a solid hemicellulose citrate–chitosan sample by oven drying a wet sample after the cross linking reaction, without freeze drying. The volume was measured using a water displacement method. The pore wall density was determined to be 1.1 $\mathrm{g/cm}^3$.

3. Results and discussion

3.1. *Effect of reaction time and concentration*

The reaction time (0.5–3.0 h) and solid to liquid ratio (1:60 to 1:140) were investigated to determine optimum reaction conditions. For these experiments, the hemicellulose citrate:chitosan ratio was 1:1, pH 3.5 and reaction temperature 110 °C. Water and saline absorption increased with reaction time (from 510% to 1550% and 970% to 1760%, respectively, with vacuum filtration method) and solid to liquid ratio (from 630% to 1420% and 1120% to 1360%, respectively, with vacuum filtration method). The weight loss decreased with increased reaction time and generally increased with the increased solid liquor ratio. The maximum water absorption and minimum weight loss were obtained at 2.5 h reaction time and solid to liquor ratio 1:100.

3.2. *Formation of aerogel foam structure*

A flexible dry aerogel foam was formed via freeze drying from hemicellulose–chitosan and hemicellulose citrate–chitosan, Fig. 3. The foam can be deformed over a large strain and when the load is removed the original shape is recovered. However, neither chitosan alone nor hemicellulose citrate alone would form foams upon

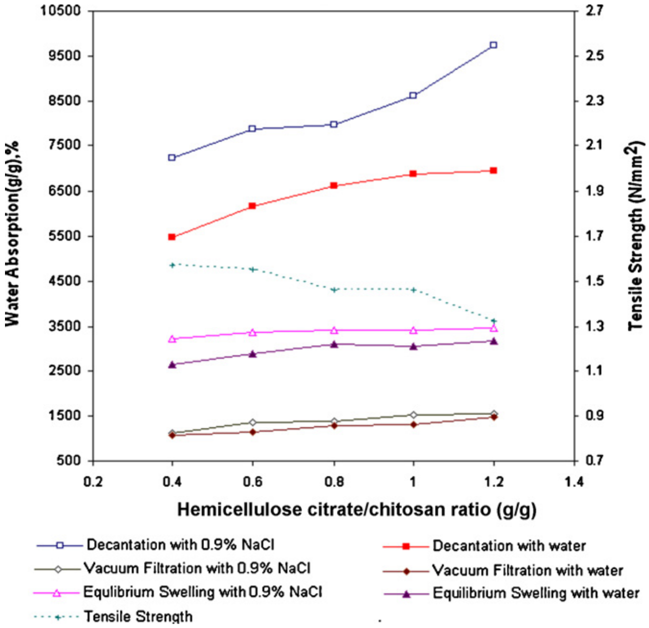

Fig. 6. Effect of hemicellulose citrate to chitosan ratio on water absorption (1 h soaking) and tensile strength. Reaction conditions: 3 h, solid to liquid ratio 1:100, pH 3.5, 110 °C.

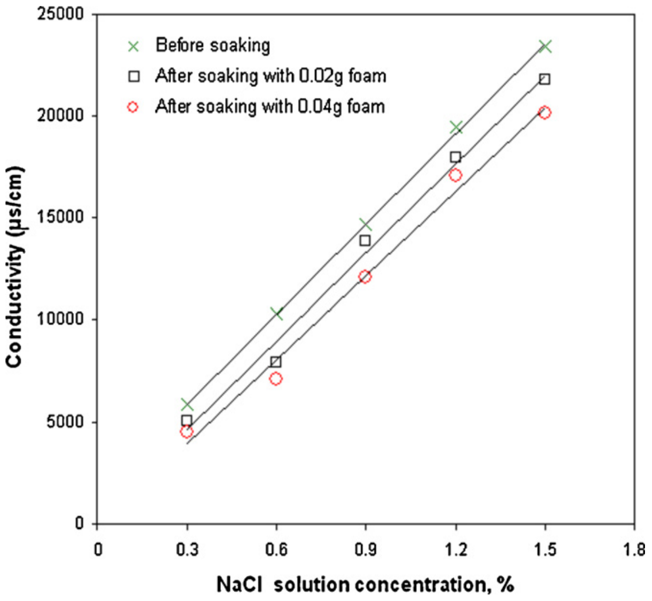

Fig. 7. Conductivity of sodium chloride solution before (×) and after soaking of 0.02 g (unfilled squares) and 0.04 g (circles) of hemicellulose citrate–chitosan foam in 50 ml of a NaCl solution. Reaction conditions: 1:1 of HC:C, 3 h, solid to liquid ratio 1:100, pH 3.5, 110 °C.

freeze drying. These materials formed a brittle hard glass condensed pellet. It is thus considered that the cross linking between the hemicellulose and chitosan is responsible for the elastic nature of the foam.

SEM images reveal the structure of the hemicellulose citrate–chitosan foam as being a connected three dimensional structure with plate like features and a continuous connected open cell foam pore structure, Fig. 4. The hemicellulose citrate–chitosan SEM images reveal a finer pore structure when compared to the hemicellulose–chitosan material.

The mechanical properties of the foam were investigated with dynamic mechanical analysis (DMA). DMA curves in tension mode from −10 °C to 200 °C at 2 °C/min at 1 Hz were acquired of hemicellulose citrate–chitosan foam and hemicellulose–chitosan foam for comparison, cf. Fig. 5. The storage modulus of hemicellulose citrate–chitosan foam was significantly higher than that of hemicellulose–chitosan foam and the tan delta lower, reflecting increased cross linking of the hemicellulose citrate to chitosan relative to the hemicellulose to chitosan and a more elastic like behavior of the material. Two transitions are apparent in both materials. The first transition spans 0 to 50 °C and the second from 100 to 200 °C. For hemicellulose citrate–chitosan, the lower peak appears to be two peaks overlapping. The elastic behavior at room temperature is in agreement with the transitions above and below room temperature.

3.3. Absorbent and salt complexing characteristics

The effects of the ratio of hemicellulose citrate to chitosan (g/g) on the absorption and tensile strength of the resulting foams are shown in Fig. 6. The water absorption increases with increased hemicellulose citrate to chitosan ratio whereas the strength decreases slightly. The hemicelluloses citrate contains ionizable carboxylic acid groups, which are hydrophilic and aid in imbibing water into the foam structure.

From titrations, it was determined that the hemicellulose citrate had approximately 742 mequiv. (acid) per 100 g of material and the chitosan had 525 mequiv. (amine) per 100 g of material. Thus, at a ratio of hemicellulose citrate to chitosan of 0.7 to 1, there is an equal amount of acid and amino groups. The absorption properties versus composition continuously increase without significant effect at the stoichiometric ratio. This implies that only a fraction of the amino and acid groups react and that a continuous increase in the hemicelluloses promotes more water uptake due to free carboxylic acid groups.

Interestingly, the saline water (0.9% NaCl solution) absorption measured with three different absorption tests was significantly higher than with the de-ionized water. This is unlike a conventional superabsorbent, which absorbs less saline solution than pure water. This increased saline absorption was also accompanied by other changes in the degree of swelling and weight loss of the foam when compared to commercial super absorbents.

Table 1 shows the swelling values, volume expansion and tensile strength for various experimental materials as well as commercial products. In comparing volume expansion for commercial super absorbent, one sees that the commercial superabsorbent expands significantly less in saline solution when compared to deionized water. This can be contrasted with hemicelluloses citrate–chitosan foam, which has a larger volume expansion in saline compared to deionized water. The increased volume expansion was to accommodate the increased saline solution uptake. The absorbency of the hemicellulose citrate–chitosan foam was significantly higher than the commercial cellulose foam with water and saline solution. This was true even though the void fraction of the commercial cellulose foam of 0.9656 was similar to the hemicellulose citrate–chitosan (in the range of 0.9978). The hemicellulose citrate–chitosan maintained a 630% saline solution absorbed under load (Table 1). This value was similar to starch citrate–chitosan (670%) and a commercial diaper product consisting of wood fibers and superabsorbent (660%). The commercial cellulose sponge had a 50% saline solution absorption under load. The higher value of hemicellulose citrate–chitosan relative to the cellulose sponge reflects a higher tenacity to hold the liquid, indicating that the chemistry of the material is influencing the affinity of liquids. This is independent of the effect of pore fractions of the materials. The superabsorbent alone had an 1160% absorbance under load, indicating a superior liquid holding performance under load relative to the hemicellulose or starch based citrate–chitosan materials.

Table 1
Properties of hemicellulose citrate–chitosan foam and other materials. Hemicellulose citrate to chitosan mass ratio 1:1, pH 3.5, 3 h, 110 °C and solid:liquor ratio 1:100. NA means hemicellulose citrate or chitosan produces a powder, not a foam.

Sample	Density (g/cm^3)	Water absorption (g/g) % with DI water 1 h			Saline absorption (g/g) % with 0.9% NaCl 1 h				Weight loss (%) at 1 h (ES)		% Volume expansion[a]		Tensile strength (N/mm^2)
		Dec	ES	VF	Dec	ES	VF	Load[b]	Water	NaCl	Water	NaCl	
Hemicellulose citrate–chitosan	0.00254	7800	3100	1500	9800	3600	1800	630	8.1	−9.3	110	240	1.61
Hemicellulose–chitosan	0.00572	2300	800	400	2400	900	400		28.6	23.7			0.54
Hemicellulose citrate		1400	500	350	1500	600	400		21.0	15.6			NA
Hemicellulose		600	200	100	700	300	200		18.5	16.2			NA
Starch citrate–chitosan	0.00406	11,300	2780	1830	13,960	3800	2440	670	7.1	−10.0	200	270	1.8
Starch–chitosan	0.00757	2320	730	530	2610	720	540		20.4	14.8			1.0
Starch		1020	800	640	930	730	610		23.1	16.3			NA
Chitosan		1200	700	600	1300	1000	600		53.0	41.0			NA
Commercial cellulose foam	0.0378	700	600	200	800	600	300	50	55.4	50.9	20	40	23.8
Super absorbent (acrylic base)		24,100	19,700	14,900	4700	4200	1800	1160	2.9	1.0	21,000	140	NA
Commercial diaper					3400			660					

[a] Volume expansivity equals 100% $(V_{eq} - V_{dry})/V_{dry}$, where V is volume and eq and dry denote liquid swollen (1 h) and dry states.
[b] Saline solution absorbance under a load of 4.9 psig. See Section 2.

In investigating the enhanced saline uptake of the hemicellulose citrate–chitosan, one possible explanation for the increase saline uptake may be that the material is acting as a polyampholyte (Bernabé, Peniche, & Argüelles-Monal, 2005; Dobrynin, Colby, & Rubinstein, 2004). In particular, the polyampholyte is created by two polymers that are crosslinked such that the resulting material has both positive and negative species on it over the pH tested. Chitosan is known to have a pKa of about 6.2 (Park, Choi, & Park, 1983). Thus, below pH of 6.2 one would except that the amine group is protonated and carrying a positive charge. The free carboxylic acid groups associated with the hemicelluloses citrate would have pKa much lower than that of chitosan. Thus, the carboxylic acid would be ionized and carrying a negative charge. These charges can interact with each other and limit swelling. Upon the addition of salt, the increased ionic strength of the solution screens the interaction of the charged groups and allows for increased swelling much like in a Zwitterionic polyampholyte (Dobrynin et al., 2004).

Sodium chloride appears to form a complex with hemicelluloses citrate–chitosan foam. This is evidenced by the conductivity of the saline solution before and after the soaking of the foam (Fig. 7). The decrease in conductivity indicates a decrease in sodium and chloride ion concentration in the solution. This can be more directly evaluated by evaporating the remaining saline solution after an absorption experiment. Table 2 shows the salt concentration before and after the absorption experiment for three different materials. From this, the salt uptake can be directly evaluated. The conductivity of the solutions was also measured. The hemicellulose citrate–chitosan material absorbed the most salt and also showed the largest drop in conductivity indicating a unique property when compared to the other materials.

Further evidence for the complex forming between the hemicelluloses citrate–chitosan foam and the sodium chloride can be found in the weight change data upon soaking in water or saline solution. Table 3 displays the change in the dry weight of the foam expressed as a percentage after soaking in deionized water and saline solution. For all of the samples soaked in deionized water, a decrease in the weight was found after soaking. This indicates that a portion of the material was dissolved and discarded with the water during the experiment. For nearly all of the saline solution samples, an increase (negative decrease) in the weight was found at a pH of 3.5. The samples that did lose mass only lost a very small amount (2.4 and 1.1%). This data, in conjunction with the decreased conductivity, indicates that the sodium chloride was forming a complex with the hemicelluloses citrate–chitosan.

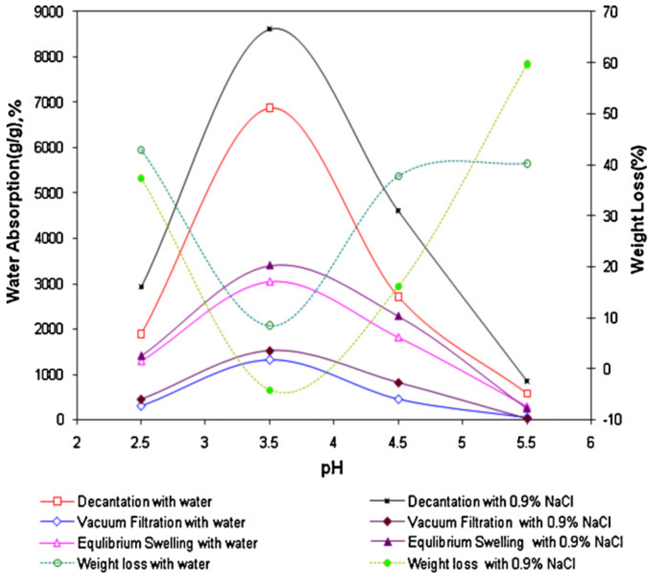

Fig. 8. Effect of reaction pH on water absorption and weight loss (1 h soaking). Reaction conditions: 1:1 of HC:C, 3 h, solid to liquid ratio 1:100, 110 °C.

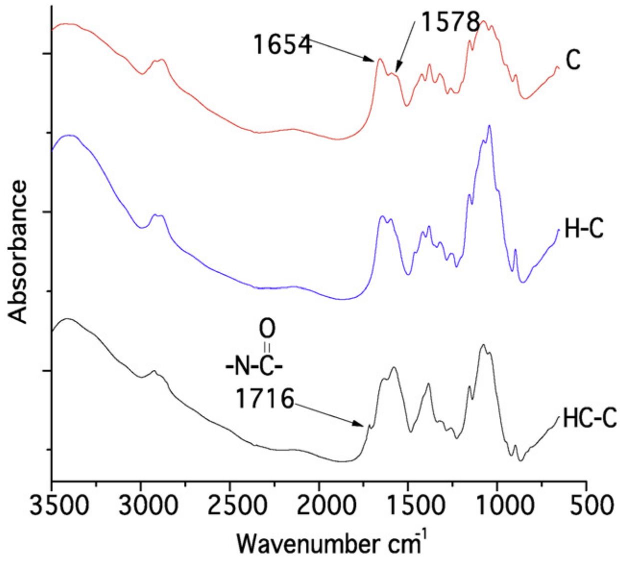

Fig. 9. FTIR spectra of (C) chitosan, (H–C) hemicellulose–chitosan and (HC–C) hemicellulose citrate–chitosan.

Table 2
Salt removal and conductivity of saline solutions before and after treatment with absorbents. Sample mass was 0.02 g and the saline solution was 50 ml volume.

Sample	Initial NaCl (g/l)	Final NaCl (g/l)	NaCl absorption (g/g)	Initial conductivity (μs/cm)	Final conductivity (μs/cm)	Reduction in conductivity (%)
Hemicellulose citrate–chitosan	9.0	8.5	0.63	13,100	10,000	24
Commercial cellulose foam	9.0	9.0	0.00	13,100	13,800	−6
Super absorbent	9.0	8.8	0.25	13,100	13,300	−2

Table 3
Effect of hemicellulose citrate to chitosan ratio on properties. NA indicates that these conditions did not produce a foam product. Weight loss measured at 1 h with equilibrium swellability method.

Hemicellulose citrate:chitosan ratio	Reaction temperature (°C)	pH	Tensile strength (N/mm^2)	Weight loss with DI water	Weight loss with 0.9% NaCl solution	Void fraction
0.4:1	100	3.5	1.57	12.6	−6.3	0.9968
0.6:1			1.55	11.7	−7.2	0.9970
0.8:1			1.46	9.6	−7.9	0.9974
1:1			1.46	7.1	−9.3	0.9976
1.2:1			1.30	17.4	2.4	0.9980
1:1	80	3.5	1.06	15.1	3.8	0.9966
	90		1.29	10.0	−4.7	0.9970
	100		1.46	8.5	−9.3	0.9975
	110		1.61	8.1	−5.3	0.9977
	120		1.30	8.7	1.1	0.9980
1:1	110	2.5	0.20	42.9	37.4	0.9922
		3.5	1.61	7.6	−5.3	0.9977
		4.5	0.79	37.8	16.1	0.9947
		5.5	NA	40.3	59.7	0.9735

In examining the effect of pH on the weight loss in Table 3, one sees that for the samples that are soaked in saline, there is a shift in the weight loss depending on the pH at which the material was formed. It should be noted that the reaction mixture was not neutralized before the forming of the foam and thus we can expect that the pH of the foam is strongly influenced by the reaction conditions. The influence of pH on the weight loss can be attributed to two factors. First, varying the pH places the material in a form that does not contribute to the cross linking of material. Second, the sensitivity of the ionization state of the amine and carboxylic acid groups to pH will change the ability of the material to form a complex as a polyampholyte. When the complex is not formed due to both the amine and carboxylic acid being in the same ionization state, the water uptake is decreased and the weight loss increased dramatically. This is illustrated in Fig. 8. It is clear from this figure that the pH of 3.5 showed the best performance of the pH tested. With both higher and lower pH showing reduced liquid uptake and increased weight loss. Additionally, using TGA, it was found that the char of the HC–C sample soaked in the NaCl solution had a weight that indicated that the sample had approximately 13.5% by weight NaCl.

To further elaborate on the interaction of hemicelluloses citrate and chitosan, the dependence of the water uptake and weigh loss on the pH suggests that the hemicelluloses citrate and chitosan are interacting through a complexing mechanism. While this may be part of the interaction and an important interaction for understanding the water uptake behavior, evidence also suggests that a covalent bond exists between the hemicelluloses and chitosan. The FTIR spectra of chitosan (A), hemicellulose–chitosan (B) and hemicellulose citrate–chitosan (C) are shown in Fig. 9. Analysis of the FTIR data for chitosan (C) showed absorption bands at 1654 and 1578 cm^{-1}, corresponding to amide (I) and amide (II) bands respectively. The bands observed at 3474 cm^{-1} correspond to the vibrational stretching of the hydroxyl groups (Nie, Tan, & Zhang, 2006). For hemicellulose citrate–chitosan (HC–C) a new peak is observed at 1716 cm^{-1}, attributable to the characteristic stretching band of carbonyl groups in an amide bond of hemicellulose citrate crosslinked with chitosan (Umemura & Kawai, 2008) in agreement with the hemicellulose citrate being linked to chitosan via reactions between amine groups of chitosan and carboxylic groups of hemicellulose citrate (Alonso et al., 2009; Edlund & Albertsson, 2008; Yin, Luo, Chen, & Khutoryanskiy, 2006). This supports the notion that hemicelluloses citrate and chitosan are covalently crosslinked to a certain extent.

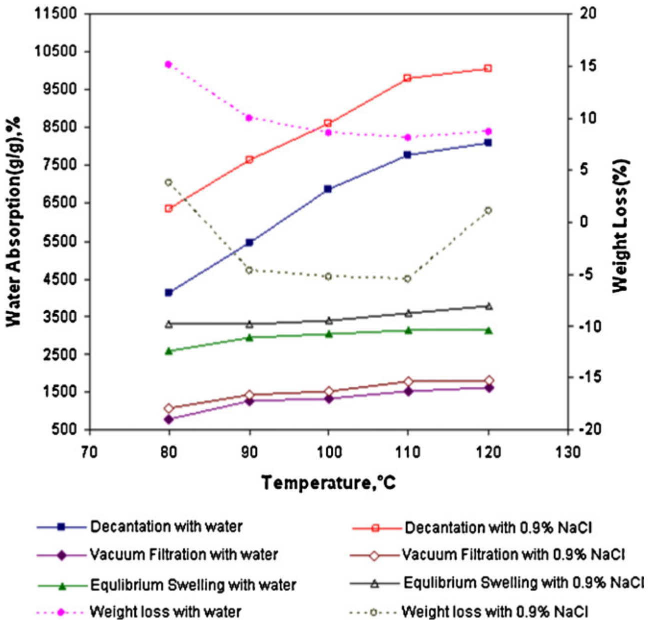

Fig. 10. Effect of reaction temperature on water absorption and weight loss (1 h soaking). Reaction conditions: 1:1 of HC:C, 3 h, solid to liquid ratio 1:100, pH 3.5, 110 °C.

Additional support for the cross linking of the two materials may be found in the material property's dependence on reaction temperature. The water and saline solution absorption increased with increased reaction temperature, cf. Fig. 10. However, the weight loss of the foam decreases with increased temperature for the deionized water, Fig. 10. It is expected that a covalent cross linking reaction would be more temperature dependent than a complex interaction. This was also noted by Rogacheva, Grishina, Zezin, and Kabanov (1983). The weight change observed for the foam in saline solution was more complicated. In general, a weight gain was observed with only the samples at the highest and lowest temperature showing weight losses. This suggests that there is a range of temperatures which promote the formation of polyampholyte type of materials which effectively complex sodium chloride.

4. Conclusions

Hemicellulose citrate–chitosan crosslinked foams may be synthesized by reacting hemicellulose citrate and chitosan in an aqueous medium. The incorporation of carboxylic acid groups into hemicellulose from reaction with citric acid followed by cross linking with chitosan greatly improves the properties relative to hemicellulose alone. It was found that that reaction temperature and pH were critical factors in creating a crosslink. The behavior of the material indicated that a complex between the primary amine and carboxylic acid group had a large influence on the behavior of the materials. A covalent bond was detected in in FT-IR spectrum of the reacted material, consistent with an amidization crosslink. The crosslinked hemicellulose citrate–chitosan foam has significantly increased water and saline absorption and strength, and decreased weight loss in water and saline solution compared to hemicellulose–chitosan foam and to foams generated outside of a narrow pH range. Of the conditions investigated, the optimum conditions with respect to absorption and weight loss for the cross linking of the hemicellulose citrate–chitosan include a 2.5 h reaction time at 110 °C with 3.5 pH, a solid to liquid ratio of 1:100 and a hemicelluloses citrate to chitosan ratio of 1:1 (w/w). The hemicellulose citrate–chitosan was shown to absorb sodium chloride from a saline solution, possibly due to a salt complex similar to a polyampholyte. Overall the hemicellulose citrate–chitosan foam was found to have interesting properties including being highly elastic at room temperature, performing similar to commercial superabsorbents in saline uptake, and having the ability to complex salt from solution, thus reducing the overall salinity of the water.

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