Synthesis, and Investigation of Swelling Behavior Natural Based Superabsorbent Composites with High Thermal Resistance

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Abstract: In the present paper, attention is paid to synthesis and investigation swelling behavior of a superabsorbent hydrogel composite based on Pectin (Pec) and polyacrylonitrile (PAN) in the presence Kaolin powder. The physical mixture of Pec, Kaolin and PAN were hydrolyzed by NaOH solution to yield H-Pec-poly (sodium acrylate-co-acrylamide)/Kaolin superabsorbent hydrogel composite. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR and SEM spectroscopies respectively. According to FTIR, all the nitrile groups were converted to carboxylate and carboxamide groups. H-pectin-g-PAN/Kaolin composite was also characterized by DSC and TGA thermal methods. Both modified pectin exhibited enhanced thermal stability over pectin. On the other hand, the Pec-poly (sodium acrylate-co-acrylamide) hydrogel composite exhibited a pH-responsiveness character so that a swelling-deswelling pulsatile behavior was recorded at pHs 3 and 8. This abrupt swelling behavior was explained based on variety of pH-dependent interactions of functional groups incorporated in the gel network by an external pH modulation. The results clearly suggested that the natural-based hydrogel composite may be a potential polymeric carrier for drug delivery in the intestinal tract.

Key words: Pectin; Polyacrylonitrile; Superabsorbent, Composite, Thermal-Resistance.

INTRODUCTION

Vinyl graft copolymerization onto polysaccharide backbones is a well-known method for synthesis of natural-based superabsorbent hydrogels composite. The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile, was synthesized using this method. These biopolymer materials are crosslinked hydrophilic polymers, capable of absorbing large quantities of water, saline or physiological solutions. They are widely used in many fields such as hygienic, cosmetics, and agriculture, F.L. Buchholz and A.T. Graham, 1997; W.E. Hennink and C.F. Van Nostrum, 2002; Peppas LB and Harland RS, 1990; Po R, 1994; Hoffman AS, 1996.

Because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity, polysaccharides and proteins are the main part of the natural-based superabsorbent hydrogels. The higher production cost and low gel strength of these superabsorbers, however, restrict their application widely. To improve these limitations, inorganic compounds with low cost can be used. The introduction of inorganic fillers to a polymer matrix increases its strength and stiffness properties. Among inorganic compounds, special attention has been paid to clay minerals in the field of nanocomposites because of their small particle size and intercalation properties J. Wu et al., 2000. Mineral powders are hydrated layered aluminosilicate with reactive -OH groups on the surface. The interaction of mineral powders, reactive site of natural polymers and monomers result in a superabsorbent composite. Superabsorbent composites based on synthetic polymers, J. Lin et al., 2001; J. Wu et al., 2003; Kirk RE and Othmer DF, 1992, or natural polymers, Hsu S.C et al., 2002, have been reported.

Pectin are relatively new polysaccharides to synthesize of natural-based SAPs. Following a continuous research on modification of pectin, in this work, we attempt to synthesize and characterize new superabsorbent hydrogels based on pectin in the presence of kaolin particles. The preparation of the biopolymer-based superabsorbent composites can also improve the mechanical properties of materials and can lower the cost of the finished product compared with the synthetic counterparts as well as providing biodegradable characteristics.

Experimental

1.1. Materials:

Pectin (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). Acrylonitrile monomer (AN, Merck) was distilled before use. Kaolin powder from Fluka, particle size < 5 µm) were used as received. All other chemicals were analytical grade and used without further purification. Double distilled water was used for the hydrogel preparation and swelling measurements.
1.2. Synthesis of Superabsorbent Hydrogel Composite:
A facial one step preparative method was used for synthesis of Pec-poly (sodium acrylate-co-acrylamide)/kaolin hydrogel composite. A general procedure for alkaline hydrolysis of Pec-PAN/kaolin mixture was conducted as follows. Pectin (0.50-1.33 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath. Then, various amounts of Kaolin powder (0.25-0.75 g) were added to the pectin solution and allowed to stir (300 rpm) for 15 min. After complete dissolution of the polysaccharide and kaolin to form a homogeneous solution, certain of sodium hydroxide (0/25-2/5N) was added to the mixture at desired temperature (alkalization temperature, 20-120 °C). The mixture was allowed to stir for certain times (alkalization times, 20-90 min). The various amount of polyacrylonitrile (0.50-4.50 g) was dispersed in the reaction mixture to saponify for certain times and temperatures (alkaline time and temperature). During the saponification NH₃ gas was evolved and a color change from red to light yellow. This discoloration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8.0 by addition of 10 wt % aqueous acetic acid solution. Then the gelled product was scissored to small pieces and poured in ethanol (200 mL) to dewater for 5 h. The hardened particles were filtered and dried in oven (50 °C, 10h). After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light, A. Pourjavadi et al., 2004.

1.3. Studies of the Dynamic and Equilibrium Degree of Swelling:
The tea bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.5 ± 0.001 g) with average particle sizes between 40-60 mesh (250-350 μm) was immersed entirely in distilled water (200 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The equilibrated swelling (ES) was measured twice using the following equation:

\[
ES(\text{g/g}) = \frac{\text{Weight of swollen gel} - \text{Weight of dried gel}}{\text{Weight of dried gel}}
\]  

The accuracy of the measurements was ±3%.

1.4. Instrumental Analysis:
Fourier transform infrared (FTIR) spectroscopy absorption spectra of samples were taken in KBr pellets, using an ABB BOMEM MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature. The surface morphology of the composite was examined using scanning electron microscopy (SEM). After Soxhlet extraction with methanol for 24 h and drying in an oven, superabsorbent powder was coated with a thin layer of gold and imaged in a SEM instrument (Leo, 1455 VP).

1.5. Thermal Analysis:
A simultaneous thermal analyzer (STA-625, Reometric Scientific) was used for differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under nitrogen. The heating rate was 2 0°C/min.

RESULTS AND DISCUSSION

Mechanism of Hydrogel Formation and IR Analysis:
A general reaction mechanism for H-Pec-poly (AN)/kaolin hydrogel composite formation is shown in Scheme 1. At the first step, hydroxyl groups of Pectin substrate was converted to corresponding alkoxide ions using sodium hydroxide solution. Then, these macroalkoxides initiate crosslinking reaction between some adjacent polyacrylonitrile pendant chains. This reaction leads to intermediate formation of naphthyridine cyclic structures (including imine, -C = N-, conjugated bonds) with deep red color. The intermediate was then hydrolyzed using residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups (Scheme 1) with a resulting color change from red to light yellow. This sharp color change was used as an indication to halt the alkaline treatment. However, incompletely hydrolyzed structures may also give rise to a few crosslinking points result in a loosely crosslinked network. It has been reported, in the case of H-SPAN, a maximum conversion of 70% of nitrile to carboxyl groups and the remaining 30% are amide groups, Barbucci R et al., 2000. In fact, details of the chemical processes and mechanism involved in H-SPAN synthesis are not yet well understood. For instance, the incomplete hydrolysis is interpreted as being related to steric and polar factors, Lim DW et al., 2001. Weaver et al. suggested that condensation might also occur between carboxyl and amide groups to form imide structures, Barbucci R et al., 2000. Therefore, in the case of our hydrogel composite, Pec-poly (NaAA-co-AAm)/kaolin, we realized that precise control of the ratio is practically impossible.
Scheme 1: Proposed mechanism for crosslinking during the hydrolysis of nitrile groups of the Pec–PAN mixture to produce the H-Pec-poly(NaAA-co-AAm)/kaolin composite.

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel composite. Figure 1 shows the FTIR spectra of Pec-PAN physical mixture and the resulted hydrogel composite, Pec-poly(NaAA-co-AAm)/kaolin. The band observed at 2242 cm⁻¹ can be attributed to stretching of -CN group of polyacrylonitrile (Fig. 1b). The hydrogel comprise an Pectin backbone with side chains that carry carboxamide and carboxylate functional groups that are evidenced by three new peaks at 1407, 1556, and 1675 cm⁻¹ (Fig. 1c). These peaks attributed to C = O stretching in carboxamide functional groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively, A. Pourjavadi et al., 2004. The stretching band of -NH overlapped with the -OH stretching band of the Pectin portion of the copolymer. As shown in Fig. 1c and Scheme 1, after alkaline hydrolysis, most of the nitrile groups are converted to carboxamide and carboxylate groups.

To obtain an additional evidence of in situ crosslinking during alkaline hydrolysis, a similar reaction was conducted in absence of the polysaccharide. Since the resulted product became soluble, the crosslinks really formed between the alkoxide ions of Pectin and the nitrile groups of PAN. This fact practically proves that the pectin hydroxyls are involved in the crosslinking.

In IR spectrum of the hydrogel composite (Fig. 1c), the absorption band at 1707 cm⁻¹ can be corresponding to the ester groups that can be formed during the graft polymerization reaction. The carboxylate groups of the graft can be react with the -OH groups on the kaolin surface. The replacement of -OH groups in the surface of kaolin by carboxylate anions results in the ester formation. As shown in figure 1c, the absorption bands of -OH of kaolin at 3628-3674 cm⁻¹ are disappeared, Silverstein RM, 1998.

**Scanning Electron Microscopy:**

One of the most important properties that must be considered is hydrogel composite microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Figure 2c shows an SEM micrograph of the polymeric hydrogel composite (H-Pec-poly(NaAA-co-AAm)/kaolin) obtained from the fracture surface. The hydrogel composites have a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimulis with the hydrophilic groups of the graft copolymers.
**Fig. 1:** FTIR spectra of (a) Pectin, (b) Pectin-g-poly(AN), (c) H-Pectin-g-poly(AN)/Kaolin hydrogel composite.

**Fig. 2:** SEM photograph of the pectin (a), and H-Pec-poly(NaAA-co-AAm)/kaolin hydrogel composite Surfaces (b).
Thermal Characterization:

DSC and TGA traces are presented in Figure 3. The initial pectin exhibits two distinct weight losses in its thermogravimetric curve. The one in the range of 40-168°C, peaking at 90.9°C, is associated with loss of water (6.6 wt %), and the other in the range 270-363°C, with maximum decomposition rate at 325°C, has been ascribed elsewhere.

Grafting of polyacrylonitrile makes the pectin hydrophobic. A weak endothermic transition in DSC (curve b, 70.5°C) and a little absorbed water in TGA (curve b, the first weight loss 2.5 wt %) indicate that the graft copolymer pectin-g-PolyAN is much more hydrophobic than the other polymers. Conversely, the H-Pec-poly (NaAA-co-AAm)/kaolin composite shows a large amount of absorbed moisture (TGA curve c, 13.2% weight loss; DSC curve c, intense endothermic peak at 90.6°C). Details of the thermal analysis data are summarized in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DSC</th>
<th>TGA</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Temp., °C</td>
<td>T&lt;sub&gt;f&lt;/sub&gt;, °C</td>
</tr>
<tr>
<td>Pectin</td>
<td>70.8 [+33.0] [340.6-383.1] 418.0 [-52.7]</td>
<td>90.9 [6.1%]</td>
</tr>
<tr>
<td>H-Pectin-g-PAN</td>
<td>70.5 [Negligible] 338.0 [-752.0]</td>
<td>75.2 [2.5%]</td>
</tr>
<tr>
<td>H-Pectin-g-PAN/Kaolin composite</td>
<td>90.6 [+119.0] 267.6 [+54.1] 316.0 [+11.7] 375.0(NM) 454.0(-71.4)</td>
<td>66.2 [13.5%]</td>
</tr>
</tbody>
</table>

a Enthalpy change, + : endothermic, - : exothermic.
b Temperature at the first weight loss of the corresponding peak of the DTG curve.
c The first weight loss, wt %
d Integral procedural decomposition temperature.
e Nonmeasurable by the instrument.

IPDT (integral procedural decomposition temperature), as a means of summing up the whole shape of the normalized data curve of TGA, was also calculated to get a more semiquantitative data regarding the relative thermal stabilities. Overall, according to the char yield and IPDT values, thermal stability of both grafted copolymer and hydrogel composite is improved in comparison with pure pectin itself, Doyle, C.D, 1961. It may be attributed to formation of conjugated cyclic systems consisting -C=N- groups from the pyrolytic addition reaction of adjacent nitrile groups in the case of pectin-g-PolyAN. The important feature of this conjugation is the sudden evolution of a large amount of heat (752.4 J/g). Although there is no nitrile group in H-Pec-poly (NaAA-co-AAm)/kaolin structure, the existence of COONa, COOH, and CONH<sub>2</sub> groups improve its thermal stability (IPDT 448°C) over pectin. These various groups of the synthetic part as well as the functional groups of the polysaccharide part, i.e., NH₂, NH₃, NHCOCH₃, and OH, participate in a variety of reactions upon heating. In the DSC cure of the H-Pec-poly (NaAA-co-AAm)/kaolin composite, four distinct endothermic peaks are observed. The first peak (H 119.0 J/g) is due to the evaporation of absorbed water in the sample. The second peak (H 54.1 J/g) at temperature 267.9°C may be attributed to evolution of ammonia by the formation of imide group via cyclization. The third endothermic peak is probably due to decacylation of pectin moieties, because a part of polycrylic carboxylic groups are forming salt bands with the amino groups of pectin sections, and therefore are not susceptible to degradation by dehydration and decarboxylation reactions as normal polycrylic acids do, Doyle, C.D, 1961.

The fourth endothermic peak (375.0°C) may be related to decarboxylation. The last enthalpy change starts above 400°C and extends to 500°C, with a maximum decomposition rate around 454.6°C (exothermic, H ≈ -71.4 J/g). It corresponds mainly to the degradation of the polycrylic chains and rarely to the decomposition of the rest of the saccharide backbone.

Effect of pH on the Swelling Capacity:

In Figure 4 the equilibrium swelling of the hydrogel composite is presented as a function of pH (ranged from 1 to 12). No additional ions (through buffer solution) were added to medium for setting pH because absorbency of a superabsorbent is strongly affected by ionic strength. Therefore, stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.
The hydrogel composite contained -CO₂H, -COO⁻, and -CONH₂ groups related to hydrolyzed grafted poly (AN) monomers. These groups are very acidic and fast ionizable. As shown in Fig. 4, the swelling of the hydrogel composite is increased up to pH 8. Low swelling of the hydrogel composite in very acidic conditions may be attributed to the screening effect of the counter ions, i.e. Cl⁻, shields the charge of the carboxylate anions and prevents an efficient repulsion. As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). With increasing of the pH, the ionic strength of the solution (shielding effect of Cl⁻) is decreased and the swelling increased. At pH 8, the high the anion-anion repulsive electrostatic forces of - carboxylate groups, the high swelling will be. Above pH 8 the swelling is decreased that it can be attributed to screening effect of the counter ions, i.e. Na⁺, shields the charge of the carboxylate anions and prevents an efficient repulsion, G. R. Mahdavinia et al., 2004; Chen J and Zhao Y, 2000; Flefel, E.M et al., 2002.
pH-Responsiveness Behavior of H-Pec-poly(NaAA-co-AAm)/Kaolin Composite

Since the present hydrogel composite show different swelling behaviors in acidic and basic pH solutions, we investigated the reversible swelling-deswelling behavior of these hydrogels composite in 0.01 M solutions at pH 2.0 and 8.0 (Figure 5). At pH 8.0, the hydrogel composite swells due to anion-anion repulsive electrostatic forces, while at pH 2.0, it shrinks within a few minutes due to protonation of the \(-\text{CO}_2\) anions. This swelling-deswelling behavior of the hydrogels composite makes them as suitable candidate for designing drug delivery systems. Such on-off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels, Ibrahim, M.M et al., 2002. Again, a screening effect of the counter ions (Na\(^+\)) limits the swelling at pHs 9-13.

![Fig. 5: The pH-responsiveness behavior of H-Pec-poly(NaAA-co-AAm)/kaolin composite in solutions with pH 2.0 and 8.0.](image)

Swelling Behavior of Hydrogel Composite in Salt Solutions:

Changing of environmental ionic strength affects significantly the swelling capacity of hydrogel composite. Figure 6 shows the effect of the various salt solutions with various concentrations on the water absorbency of H-Pec-poly (NaAA-co-AAm) /kaolin composite. The decrease of the swelling capacity of the hydrogel composite is due to the screening effect and a loss of the osmotic pressure difference between the hydrogels composite and the fluids. The H-Pec-poly (NaAA-co-AAm) /kaolin composite comprise carboxylate groups in their structures. In salt solutions, the perfect anion-anion repulsion of the carboxylate groups is prevented by the Mn\(^+\) cations that shield the carboxylate groups, so the swelling capacity is decreased, Berlin, A.A and Kislenco, 1992. In addition, the swelling of the hydrogel composite depends on the valency of the cations. Multivalent cations decrease drastically the swelling capacity. The decrease is attributed to the complexing ability of carboxylate groups inducing interchain complexes formation and consequent enhancing of the network crosslink density, Pourjavadi, A. and Zohuriaan-Mehr, M.J, 2002. The composite comprises carboxylate anions (\(-\text{COO}^-\)). The water absorbency of the composite in the presence of the Ca\(^+\) and Al\(^{3+}\) cations is lower than that of NaCl solution. This phenomenon is arisen from ionic crosslinking of these cations with carboxylate anions that causes low water absorbency. As arises from the results, the swelling of the composite, especially in salt solutions, is higher than that of its non-composite counterpart. The swelling improvement may be attributed to attraction of the salt cations on the surface of Kaolin in the hydrogel composite that results in lower screening effect in the composite comparing with the similar Kaolin-free sample. The reason for this anti-salt behavior can be explained as follows: the pectin-containing networks comprise carboxylate functional groups. The COO\(^-\) groups can be dissociated in aqueous media more readily than other groups of the synthetic part of the hydrogels composite. Therefore, the carboxylate ions do not keep cations in their vicinity, so the charge screening effect is not very effective. Similar conclusions are recently reported by Barbucci R, et al., 2000 in the case of a sulfated carboxymethylcellulose hydrogel. They attributed the enhanced absorbency in saline solutions to increased charge density and ionization tendency brought about by the introduction of sulfate anions.
Conclusion:

The hydrogel composite, H-Pec-poly (NaAA-co-AAm) /kaolin, was synthesized through alkaline hydrolysis of Pectin-PAN physical mixture and Kaolin powder. The reaction of Pectin alkoxide anions with nitrile groups of polyacrylonitrile, forms crosslinking points and results in a three-dimensional network. Because a polymerization reaction is not involved, so there is no need to initiator, toxic and/or expensive monomer and crosslinker. Therefore, problems such as polymerization control, conversion loss, and residual monomer are eliminated. Indeed, since no toxics material is used for the synthesis, this practical approach may be preferred to as a relatively "green process". On the other hand, the hydrogels composite exhibited high sensitivity to pH, so that, several swelling changes of the hydrogels composite were also observed in pH variations of a wide range (1-13). Ionic repulsion between charged groups incorporated in the gel matrix by an external pH modulation could be assumed as the main driving force responsible for such abrupt swelling changes. Furthermore, the reversible swelling-deswelling behavior in solutions with acidic and basic pH makes the hydrogels composite a suitable candidate for controlled drug delivery systems.

Also swelling measurement of the synthesized composites in different salt solutions showed appreciable swelling capacity, especially in NaCl solution, due to an anti-salt characteristic originated mainly from the pectin part carboxylate groups of the hydrogel composite network. Overall, we report a crosslinking polymerization to achieve superabsorbing composite materials with lower cost and lower salt-sensitivity. The hydrogel composites will most probably posses higher biodegradability (due to the pectin part) and higher swollen gel strength (due to the inorganic parts). The latter properties are of the subjects under consideration in our laboratory.

Fig. 6: Swelling capacity variation of superabsorbent composite (containing 8 wt % pectin and 1.2 wt % Kaolin) in different saline solutions with various concentrations in Multivalent cations (a) and divalent cations (b).
REFERENCES