Polyaniline – Carrageenan - Polyvinyl Alcohol Composite Material Synthesized Via Interfacial Polymerization, its Morphological Characteristics and Enhanced Solubility in Water

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Abstract. In recent years, conducting polyaniline (PAni) has been a popular interest of research in the field of conducting polymers due to its relatively low cost, ease of production, good conductivity, and environmental stability. Many studies however, have focused on improving its shortcomings such as its limited processability and solubility in common solvents. In this study, PAni, soluble in water was produced via interfacial polymerization with chloroform as the organic solvent. Poly(vinyl alcohol) (PVA) and kappa(κ), iota(ι) and lambda(λ) - carrageenan (κCGN, ιCGN, λCGN) were added to the aqueous layer to stabilize PAni in the medium. FTIR and UV-Vis absorption spectra of the solutions as well as the fabricated film confirmed the existence of PAni emeraldine salt (PAni-ES). FTIR spectrum also confirmed the peaks corresponding to the interaction of PAni with the CGNs. Moreover, PVA-CGN played a very large role on the stability of the PAni nanofibers integrated on the PVA-CGN matrix. The morphologies of the products were further investigated using SEM and TEM. Polymer electrolyte for supercapacitor or an interfacial layer for organic solar cell is being targeted as potential application of the synthesized water soluble PAni.

1. Introduction
Since the discovery of intrinsically conducting polymers (ICPs) in the 1970’s, the field has been an attractive area of research. Tens of thousands of published works on ICPs have already been produced. The study of ICPs has been popular due to their conductivities in the semiconductor range. Applications in electronics, energy, membranes, and sensors have also greatly contributed to the increase in studies of ICPs[1].

One of the most studied ICPs is polyaniline (PAni). Unlike other ICPs, PAni can exist in three forms depending on the degree of oxidation. Each degree of oxidation has different property and a characteristic color. PAni has attracted much attention due to these behaviors and due to its good conductivity, good environmental stability, relatively low cost, and facile synthesis. Similar to many other ICPs however, PAni is limited by its poor processability and solubility in common solvents [2].

Previous studies have shown that PAni can be stabilized by blending with thermoplastic polymers such poly(vinyl alcohol) (PVA)[3], poly(ethylene oxide) (PEO)[4], and poly(ethyl acrylate) (PEA)[5].
It has also been proposed that in the presence of high molecular weight anionic polysaccharides such as carrageenan[6] and chitosan[7], ionic interactions between PANi and the water-soluble polysaccharide improve the dispersibility of the PANi-polysaccharide composite in water. By interfacial synthesis, it has been observed that PANi nanofibers can be dispersed in water without the use of templates and retain good electrochemical performance [8].

This study was undertaken to improve the solubility of PANi in water by using relatively inexpensive materials and simple methods of synthesis. In this study, water-soluble PANi was synthesized by interfacial polymerization. The organic layer consisted of aniline dissolved in chloroform. Poly(vinyl alcohol) (PVA) and carrageenan (CGN) dissolved in 1.0 M HCl comprised the aqueous layer to provide a stable matrix for the PANi polymerization during interfacial synthesis. The primary objective was to graft the hydrophilic emeraldine salt form of PANi onto the water-soluble PVA-CGN matrix by ionic interactions between PANi and CGN.

2. Methodology

2.1 Materials
Ammonium persulfate (APS, 98%), ethanol (EtOH, 99.9%), and PVA (99-99.8%) were purchased from J.T. Baker. Chloroform (99.8%) was purchased from RCI Labscan. Aniline was purchased from Sigma Aldrich. HCl (36-38%) was purchased from UniChem

2.2 Interfacial Polymerization of PANi into a CGN-PVA Matrix
In the interfacial synthesis of PANi, the molar ratio between aniline and APS was kept at 4:1 with equal volumes of aqueous and organic phase. In order to maximize interactions between PANi and CGN, $\text{\l}$-CGN was used instead of $\text{\kappa}$-CGN.

In the synthesis described in this section, 0.15 g of $\text{\l}$-CGN was used in order to maintain the same molar concentration of repeating CGN units. The interfacial synthesis of PANi was studied with PVA only, $\text{\l}$-CGN only, with PVA and $\text{\l}$-CGN, and without PVA or $\text{\l}$-CGN. The aqueous solutions were prepared by dissolving the components in 30 mL of deionized water at 90°C with vigorous stirring for 1 hour. After dissolution of $\text{\l}$-CGN and PVA, the solution was allowed to cool prior to addition of 0.9 g of APS with sonication. It was observed that APS reacts with CGN on heating. Allowing the solution to cool first prevents the reaction from occurring. Organic phase was prepared by dissolving aniline in 30 mL of chloroform under sonication. The organic and aqueous solutions were allowed to cool in an ice bath before the aqueous phase was carefully poured onto the organic phase. The setups were kept under refrigeration without agitation for 18 hours. The setups were vacuum filtered with Whatman 40 filter paper then subsequently washed with EtOH, HCl, and deionized water. The precipitates were then dried in a vacuum oven at 60°C for 24 hours. Due to the small particle size of the PANi from Int-PANi-CGN-PVA, no precipitates were recovered from the solution. Instead, 5 mL of the filtrate was cast on a petri dish and dried in a vacuum oven at 60°C for 24 hours.
3. Results and Discussion

3.1 Fourier Transform Infrared Spectroscopy

IR spectra of Int-PAni-κCGN-PVA-Cast, Int-PAni-ιCGN-PVA-Cast, and Int-PAni-λCGN-PVA-Cast display similar peaks at the same positions as shown in Figure 1. All characteristic bands of PAni and the CGNs are observed. From the IR data, all three components interact similarly regardless of the type of CGN used. The spectra of the types of CGNs display similar characteristic peaks and they only differ by their of SO$_4$ peaks. κ-CGN has one peak corresponding to the 4-sulfate galactose functional group, ι-CGN has two peaks corresponding to its 4-sulfate galactose and 2-sulfate-3,6-anhydrogalactose, and λ-CGN has two peaks corresponding to its 2-sulfate galactose and 6-sulfate galactose. All the SO$_4$ peaks occur between 800 cm$^{-1}$ to 850 cm$^{-1}$. In the composites however, no sulfate bands are detectable since they overlap with the out-of-plane C-H deformation on the 1,4-disubstituted benzene ring of PAni which are found within the same range, but with greater intensities. The broad O-H band of CGN also significantly decreased in intensity in the composites. Relative to the other bands, the bands of the N-H$^+$ stretches, the polaron band, in the C-H plane of the composites are relatively prominent. Longer bond length is associated with greater band intensities, suggesting interactions between the PAni N-H$^+$ and the CGNs. The summary of the identified peaks and their corresponding interpretations is presented in Table 1.

Table 1. Position of characteristic FTIR peaks of (a) Int-PAni-κCGN-PVA, (b) Int-PAni-ιCGN-PVA, and (c) Int-PAni-λCGN-PVA

| Bands                                      | a   | b   | c   |
|--------------------------------------------|-----|-----|-----|
| CGN O-H stretch of water recrystallization | 1680| 1660| 1650|
| Sulfate symmetric and asymmetric vibrations| 1375| 1376| 1374|
|                                          | 917 | 912 | 913 |
| Galactose C-O and C-O-C vibrations        | 1041| 1042| 1043|
| Quinoid deformation                       | 1563| 1567| 1560|
| Benzenoid deformation                     | 1505| 1505| 1505|
| C-N stretch                               | 1312| 1304| 1316|
| N-H$^+$ stretch in C-H plane              | 1138| 1134| 1140|
| Out-of-plane C-H deformation on 1,4-      | 821 | 823 | 818 |
| disubstituted benzene ring                |     |     |     |
| C-N$^+$ stretch                           | 1235| 1242| 1235|
| Composites O-H and N-H Interactions       | 2600| 2588| 2599|

Figure 1. IR Spectra of (a) Int-PAni-κCGN-PVA-Cast, (b) Int-PAni-ιCGN-PVA-Cast, and (c) Int-PAni-λCGN-PVA-Cast
3.2 Scanning Electron Microscopy
The SEM images of the samples showed varying degrees of homogeneity among the samples as shown in Figure 2. Int-PANI-$\kappa$CGN-PVA, had a smooth morphology, the surface appears to be relatively uniform and smooth. Smooth surfaces are characteristic of blends with good homogeneity. Int-PANI-$\iota$CGN-PVA had fibrous morphology but the fibers fused together as the film dried. Fusion of one-dimensional structures is characteristic of the formation of three-dimensional PANi structures. It was observed that granules formed on top of the fibrous surface. PVA inherently forms smooth flakes while PANi forms granules in an inhomogeneous blend. It can then be said that Int-PANI-$\lambda$CGN-PVA cast had poor homogeneity compared to the other two samples due to the separation of PANi from the matrix. The image produced was expected since only $\kappa$-CGN and $\iota$-CGN are able to form fibers in their pure form. The $\lambda$-CGN cannot form fibers due to the steric hindrance induced by its three sulfate groups.

![Figure 2. SEM Images directly casted from an aqueous layer containing (a) $\kappa$CGN, (b) $\iota$CGN, and (c) $\lambda$CGN](image)

Shown in Figure 3 are the SEM images of the composite film after soaking it in ethanol.

![Figure 3. SEM Images After Ethanol Soaking of (a) Int-PANI-$\kappa$CGN-PVA at x3.0k (top) and x10.0k (bottom), (b) Int-PANI-$\iota$CGN-PVA at x1.0k (top) and x5.0k (bottom), and (c) Int-PANI-$\lambda$CGN-PVA at x5.0k (top) and x10.0k (bottom)](image)

The SEM image of Int-PANI-$\kappa$CGN-PVA showed a granular morphology. The smooth flakes associated with PVA were not visible at the surface of the film. In Int-PANI-$\kappa$CGN-PVA, the PANi
agglomerated on the surface of the PVA fibers. The SEM image of Int-PAni-κCGN-PVA, Figure 3a showed a granular morphology. The smooth flakes associated with PVA were not visible at the surface of the film. In Int-PAni-κCGN-PVA, the PAni agglomerated on the surface of the PVA fibers. The SEM image of Int-PAni-λCGN-PVA, Figure 3c showed two distinct morphologies, similar to Int-PAni-λCGN-PVA-Cast. The smooth surface of the PVA is clearly seen underneath the PAni granules. Additionally, the sizes of the granules were less uniform than those of Int-PAni-κCGN-PVA. The SEM images of both interfacially polymerized samples containing λ-CGN indicate that it is not suitable for obtaining homogeneous composites with PAni and PVA. The most distinct morphology had been obtained from Int-PAni-ιCGN-PVA, Figure 3b. The image shows the cross-section of the film and part of the film’s surface at the upper portion of the image. The edges of the fibers appeared clearly in the cross-section, while the surface of the film appeared smooth and void of any nanostructures. During drying therefore, the individual fibers aligned parallel to each other and self-assembled into planar sheets. The planar sheets then stacked on top of each other to produce the film.

3.3 UV-Vis and Solubility

Scraping 20 mg off from the films and dissolving in 30 mL of deionized water with vigorous stirring produced green solutions that remained green after filtration. The absorbance bands shown in Figure 4 at 429 nm, 424 nm, and 440 nm, confirmed the presence of the benzenoid transition in the Int-PAni-κCGN-PVA, Int-PAni-ιCGN-PVA, and Int-PAni-λCGN-PVA, respectively. Bands at 860 nm, 825 nm, and 864 nm confirm the presence of the polaron transition in the Int-PAni-κCGN-PVA, Int-PAni-ιCGN-PVA, and Int-PAni-λCGN-PVA, respectively. The presence of both transitions confirmed that the solutions of the dissolved films contain PAni emeraldine salt, the conducting form of PAni. Shown in the insets in Figure 4 are the photographs of the composite material that was dissolved in water. It has been observed that the particles are uniformly dispersed in the solvents and that a clear green solution was observed. This uniform dispersability indicates that the synthesized composite is highly soluble in water. However, this research only guarantees the solubility of the composite material to 0.67mg/mL as tested.

![Figure 4. Absorbance Spectra (a) Int-PAni-κCGN-PVA, (b) Int-PAni-ιCGN-PVA, and (c) Int-PAni-λCGN-PVA, insets dissolved Solutions of (a) Int-PAni-κCGN-PVA, (b) Int-PAni-λCGN-PVA](image-url)
4. Conclusion
In this study, PANi was synthesized by interfacial polymerization into a CGN-PVA matrix. It was found that excessive amounts of CGN or PVA lead to the gelation of the solution. In the case of the most suitable type of CGN to be used, it was observed that i-CGN, being intermediate of κ-CGN and λ-CGN, imparted better properties when added to the aqueous matrix. κ-CGN produced composites with different morphologies when drop-casted or soaked in EtOH. Due to its inability to produce fibers, λ-CGN produced composites with poor homogeneity. In both the drop-casted and EtOH-soaked films, composites containing i-CGN were produced possessing the morphologies of aligned nanofibers that underwent self-assembly into larger structures. The high solubility of the synthesized composite material in water could pave way to the development of thin films and eventually functional devices without the use of toxic solvents.

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