Physico-chemical effects of supercritical carbon dioxide post polymerization treatment on HCl-doped polyaniline prepared via oxidative chemical polymerization

J G Fernando¹,²,⁴, R M Vequizo², M K G Odarve², B R B Sambo², A C Alguno², R M Malaluan², R T Candidato Jr.², J E Gambe², M Jabian², G J Paylaga², F R G Bagsican² and H Miyata³

¹ Physics Department, College of Science and Mathematics, Western Mindanao State University, Zamboanga City 7000, Philippines
² Department of Physics, College of Science and Mathematics, Mindanao State University-Iligan Institute of Technology, Iligan City 9200, Philippines
³ Department of Physics, Faculty of Science, Niigata University, 2-Nocho, Ikarashi, Niigata City, Japan

E-mail: jgfernando82@gmail.com

Abstract. Polyaniline films doped with varying HCl concentrations (0.2 M, 0.6 M and 1.0 M) were synthesized on glass substrates via oxidative polymerization of aniline. The films were treated with supercritical carbon dioxide (SC-CO₂) at 30 MPa and 40 °C for 30 minutes. Their structural, optical and morphological properties were studied and compared to conventionally prepared polyaniline films using FTIR analysis, UVVis spectroscopy and scanning electron microscopy. It was observed that supercritical carbon dioxide (SC-CO₂) could interact with PANI films that consequently altered the bandgaps and changed the film thickness. SC-CO₂ treatment also increased the oxidation level of polyaniline films and modified the morphology of polyaniline film doped with 1M HCl.

1. Introduction
Supercritical fluid (SF) is a peculiar material because it exhibits properties that are separately inherent to liquids and gases. For instance, it can diffuse through solids like gas and at the same time dissolve a number of substances like a liquid solvent [1]. SF’s properties (e.g., solubility, viscosity and density) can also be tuned by controlling its pressure or temperature [2], and have been exploited in synthesis [3], extraction [4] and material processing [5]. Among SF components, carbon dioxide is most widely used because it is non-toxic, less expensive and has convenient critical temperature and pressure (7.38 MPa and 31.1 °C) [6].

Supercritical carbon dioxide (SC-CO₂) has been extensively used in processing polymers resulting to improved properties or new products. The plasticization and swelling of polymers induced by SC-CO₂ makes it possible to prepare polymer blends [7], infuse additives such as dyes and metal complexes (impregnation) [8], extract contaminants [9] and modify morphology [10]. While there have been a number of studies on SC-CO₂ processing of polymeric materials, none has been reported

⁴ To whom any correspondence should be addressed.
on polyaniline. More so, the influence of SC-CO₂ on the physico-chemical properties of polyaniline has not yet been elucidated which restricts better predictability during processing.

In the present paper, we synthesized HCl-doped polyaniline film on glass substrates via chemical oxidative polymerization. The prepared films were treated with supercritical carbon dioxide and the influence of SC-CO₂ on the structure, morphology and optical property of PANI films was investigated.

2. Methodology

2.1. Synthesis
Polyaniline films on glass substrates were prepared by oxidative chemical polymerization of aniline with ammonium peroxydisulfate as oxidant in an acidic medium. Aniline and ammonium peroxydisulfate were dissolved separately in hydrochloric solutions (0.2 M, 0.6 M and 1.0 M HCl). One side of the substrate was sealed to prevent film formation on both sides of the substrate. The substrates were then placed on the reaction vessel where aniline and ammonium peroxydisulfate were mixed to start the polymerization. The samples were then removed after 30 minutes; rinsed with 0.2 m HCl, ethanol and water; dried; and removed from the attachment for SC-CO₂ treatment and characterization. Only half of the films (one film per synthesis) were treated with SC-CO₂.

2.2. Supercritical Carbon Dioxide Processing
The films were placed in the extracting chamber and treated with supercritical carbon dioxide for 30 minutes using supercritical carbon dioxide extraction machine (Akico). The pressure and temperature were maintained at 40°C and 30 MPa, respectively.

2.3. Characterization
The UV-Visible absorption spectra of the films were measured in the range 400 to 900 nm by Lambda 35 UV-Vis spectrometer (Perkin Elmer, UK). Fourier transform infrared spectra (FTIR) with a 1 cm⁻¹ resolution were obtained in the range 650-4000 cm⁻¹ by using Spectrum 100 FTIR spectrometer (Perkin Elmer, UK). The morphologies of the samples were examined using scanning electron microscope (JEOL).

3. Results and Discussion

3.1. FTIR spectra

![Figure 1. FTIR spectra of untreated (A) and SC-CO₂ treated (B) polyaniline films on glass substrates.](image-url)
The FTIR spectra of untreated polyaniline films are presented in figure 1. It shows extended absorption band above 2000 cm\(^{-1}\) which is characteristic of conducting polyaniline films. In the range 1400-1700 cm\(^{-1}\), two main bands were observed with maxima located at 1571 and 1492 cm\(^{-1}\), which are assigned to C=C stretching of the quinoid (Q) and benzenoid (B) rings, respectively [11]. A shoulder appears near the quinoid ring (1608 cm\(^{-1}\)) that corresponds to –C=C- ring stretching. This peak becomes more evident as HCl concentration increases because protonation induces conformational changes in the polymer which makes the vibration more infrared-active [12]. Below 1400 cm\(^{-1}\), the band assigned to C-N stretching of secondary aromatic amine is situated at 1303 cm\(^{-1}\). Two other bands intrinsic to conducting polyaniline were found at 1243 and 1148 cm\(^{-1}\) that correspond to C-N\(^{+}\) stretching and vibrational mode of –NH\(^+=\). A shoulder is also detected at 1333 cm\(^{-1}\). A less intense peak typical to a PANI base is noted at 1374 cm\(^{-1}\). The intense peaks in the range 650-1200 cm\(^{-1}\) are linked to the glass substrates.

For SC-CO\(_2\) treated films, the main characteristic absorption bands of polyaniline were also observed at 1571 (C=C stretching of quinoid ring), 1492 (C=C stretching of benzenoid ring), 1303 (C-N stretching of secondary aromatic amine) and 1148 cm\(^{-1}\) (vibration mode of –NH\(^+=\)). The maxima of these bands are not shifted with respect to untreated films except for the film protonated with 0.2 M HCl in which the –NH\(^+=\) band shifted by 12 cm\(^{-1}\) to 1136 cm\(^{-1}\). The presence of C-N\(^{+}\) stretching vibration band at 1248 cm\(^{-1}\) indicates that SC-CO\(_2\) treated films are also conducting like the untreated films. The band at 1248 cm\(^{-1}\) splits into a doublet for 0.2 M HCl; broadens for 0.6 M HCl and maintains its shape for 1.0 M HCl. The shoulder of C-N stretching band is unshifted for all HCl concentrations. The band at 1374 cm\(^{-1}\) corresponding to base form of polyaniline becomes less prominent. New bands were also observed near 2300 cm\(^{-1}\) and 1730 cm\(^{-1}\) in the spectra of film protonated with 0.2 M HCl. The former is attributed to asymmetric stretch of carbon dioxide [13] and the latter is associated to carbonic acid.

The bands in the region 1400-1650 cm\(^{-1}\) were normalized and deconvoluted so that the integrated intensity ratios (Q/B) of quinoid and benzenoid peaks can be compared. The Q/B ratio is a measure of the extent of oxidation of the films [14] i.e. 1 being the ideal Q/B ratio for emeraldine state. The Q/B ratios for untreated films protonated with 0.2 M, 0.6 M and 1.0 M HCL are 0.95, 0.99 and 0.95, respectively (figure 2). These values are close to unity which implies that the films are emeraldine. For SC-CO\(_2\) films, the Q/B ratios are 0.99, 1.20 and 1.02 for 0.2 M, 0.6 M and 1.0 M HCL protonation, respectively. The Q/B ratios for treated films were found higher than the untreated films suggesting that SC-CO\(_2\) at elevated pressure can remove electrons from polyaniline. Oxidation of polyaniline is known to convert benzenoid ring to quinoid ring and this accounts for higher amount of quinoid rings.

![Figure 2. Q/B ratio of untreated and SC-CO\(_2\) treated polyaniline films on glass substrates.](image-url)
3.2. UV-VIS Spectra

From the UV-VIS absorption spectra (figure 3), the thicknesses of the films were determined using the absorbance at 400 nm [15]. Untreated films synthesized with 0.2 and 0.6 M HCl are thicker than the film prepared with 1.0 M HCl (figure 4). This variation in the film thickness is linked to the relative amount of aniline and anilinium cations during the initiation period of polymerization. At low HCl concentrations, aniline molecules dominate the anilium cations and form more initiation centers on the surface of the substrates [16]. The high density of initiation centers more likely orient the PANI macromolecules to grow in the direction perpendicular to the substrates resulting to thicker films [17].

In SC-CO₂ treated films, the thickness of the films protonated with 0.6 and 1.0 M HCl decreased compared to untreated films. This may be due to extraction of low-molecular-weight organic intermediates and oligomers or even degradation of the polymer matrix. On the contrary, the thickness of the film with lowest HCl concentration increased after it was treated with SC-CO₂. We propose that this effect is due to dissolution of SC-CO₂ in the polymer matrix that caused it to swell[2].

Despite having the least thickness among untreated films, the film protonated with 1.0 M HCl has the highest absorbance in the range 800 to 900 nm. This suggests that the film is highly protonated since the absorption at longer wavelength is linked to the presence of polarons [18]. As expected, the film protonated with 0.2 M HCl shows the least absorbance in 800-900 nm range indicating the least level of protonation among the samples. The presence of a peak near 420 nm (polaron-π* transition), one of the characteristic peaks of polyaniline emeraldine salt, verifies the protonation of the films.
Figure 5. Plot of $(\alpha \nu)^2$ versus photon energy for PANI films doped with 0.2 M (A), 0.6 M (B), and 1.0 M (C) HCl. Dashed lines are the extrapolated lines from which the bandgaps were determined.

Similarly, SC-CO$_2$ treated films exhibit high absorbance in the range 800-900 nm implying that the films remained protonated after the treatment. The rise/drop of absorbance with respect to untreated films in this range is thickness related since it coincides directly with the change in absorbance at 400 nm.

Figure 6. Bandgaps of untreated and SC-CO$_2$ treated films doped with HCl at different molarities.

The energy bandgaps were determined from the absorption spectra using the Tauc relation

$$(\alpha \nu)^2 = A(h\nu - E_g),$$

where $A$ is a constant, $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy and $E_g$ is the bandgap [19]. The plot of $(\alpha \nu)^2$ against the photon energy and the extrapolated linear part of the graph are shown in figure 5. The bandgaps of untreated films (2.241, 2.337 and 2.406 eV for 0.2, 0.6 and 1.0M HCl, respectively) are close to the reported experimental value (2.21 eV) for doped polyaniline [20] and seen to increase with increasing HCl concentration (figure 6). This transition energy is recognized as the electronic excitation to the polaron band [21].

The bandgaps of SC-CO$_2$ treated films protonated with higher HCl molarities (2.297 and 2.330) tend to be lower than that of untreated films (figure 6) due to their enhanced quinoid character. The quinoid form has weaker resonance effect that allows electronic transitions more readily than the aromatic form [22]. However, the bandgap of the film doped with 0.2 M HCl increased to 2.277 eV.
that may be due to stronger interaction of carbon dioxide with the polymer chains. Carbon dioxide may have interacted with the polymer via the N-H structure that leads to modification of the polymer structure [11].

3.3. Morphology

![Figure 7. SEM images of untreated (a) and SC-CO2 treated (b) PANI films doped with 0.2 M HCl.](image)

![Figure 8. SEM images of untreated (a) and SC-CO2 treated (b) PANI films doped with 0.6 M HCl.](image)

![Figure 9. SEM images of untreated (a) and SC-CO2 treated (b) PANI films doped with 1.0 M HCl.](image)

SEM micrographs of untreated films reveal that their surfaces are not entirely smooth due to the presence of precipitates adhering on the grown film. All untreated films completely covered the glass substrates except for 0.2 M HCl, i.e., a small portion of the film displays nanostructures that are not well knitted. A mixture of dendritic nanorods and granular nanostructures were observed on the surface of the film protonated with 0.6 M HCl and circular patches composing of granular nanostructures in 1.0 M HCl.
The precipitates still appear on the surface of the films after they were treated with SC- 
CO2 which suggests the inability of the treatment to remove these agglomerates. The loosely knitted 
nanostructures in 0.2 M HCl film were replaced with continuous film that completely covered the 
substrate. This may support our claim that SC-CO2 can reorganize the polymer chains. Voids began to 
appear in films protonated with 0.6 M HCl and its density (2.4x10^6/cm^2) drastically increased in 1.0 M 
HCl protonated film. These observations seem to suggest that the surface quality of the film protonated 
with high HCl concentration deteriorates when treated with SC-CO2.

4. Conclusion
Post-polymerization SC-CO2 treatment was shown to affect the physical and chemical properties of 
HCl-doped polyaniline films on glass substrates. The treatment tends to decrease the thickness of the 
films synthesized using high HCl molarities and increase the thickness for low molarity. The bandgaps 
were also altered and the quinoid characters of the films were enhanced after the treatment. Voids were 
formed on the surface of the treated film doped with 1.0 M HCl.

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