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**DEVELOPMENT OF CONDUCTING  
POLYMER-BASED ANTIOXIDANT  
PACKAGING MATERIALS**

**CHYONG FANG HSU**

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*This thesis is submitted in fulfilment of the requirements for the  
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## Abstract

Antioxidants are commonly used as preservatives for protecting foodstuffs from oxidation. Packaging is believed not only to increase the economic value of products but also improve their qualities. Conducting polymers (CPs), such as soluble polyaniline and soluble polypyrrole, have been reported to exhibit antioxidant activity. Development of conducting polymer containing packaging materials, with antioxidant properties, is therefore the focus of this project. Polypyrrole (PPy), polyaniline (PANI) and poly (3,4-ethylenedioxythiophene) (PEDOT) powders were prepared using various amounts of the oxidant ammonium persulfate (APS). Spectroscopic methods, including IR and Raman, were used to identify the structures of the CP powders synthesized at various APS levels. It was found that a high level of APS led to overoxidation of the CP powders. The conductivity and doping level of the CP powders formed using higher concentrations of the APS oxidant were found to be lower than those prepared using low concentrations of APS, which might be due to overoxidation, damaging the CP structures during the preparation processes.

The antioxidant activity of PPy, PANI and PEDOT powders were evaluated using the DPPH and ABTS assays. The results showed that CP powders synthesized at a high concentration of APS presented lower free radical quenching effects, likely also due to overoxidation. The optimum initial ratio of APS to monomer for the synthesis of CP powders with a superior DPPH free radical scavenging was found to be around 0.5 for PPy, 1.5 for PANI and 1.0 for PEDOT, and the antioxidant ranking of the CP powders

was as follows: PANI1.5 > PPy0.5 > PEDOT1.0. The reduced forms of PPy, PANI and PEDOT exhibited better radical scavenging abilities than the as-prepared powders. PANI nanotubes, synthesized at high pH, was also found to exhibit stronger free radical scavenging activity than the regular granular PANI formed under acidic conditions. Structural changes of PANI powders after reaction with free radicals were observed in IR and XPS spectra, showing an increase in the ratio of imine (C=N) to amine (C-N) units.

PANI EC films were prepared using a solution method and the antioxidant capacity of the PANI EC films are examined using the ORAC assay. The results showed efficient peroxy free radical scavenging activity of the PANI EC films. A very good correlation between the ORAC response and the area of tested film was also observed, indicating a homogenous dispersion of active PANI powder across the film. Similar to the results obtained from the DPPH and ABTS assays, reduced PANI presented greater peroxy radical scavenging activity than the as-prepared powders. The influence of the PANI EC films on the oxidation of Ropufa oil was determined by peroxide value (PV) measurement. After incubation at 60°C for several days, the oil stored in the presence of the PANI EC film was found to exhibit a lower PV than in the absence of a CP film, indicating that the conducting polymer is effective in inhibiting oxidation of fish oil.

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## LIST OF SYMBOLS AND ABBREVIATIONS

A	amps
A•	antioxidant radical
AAPH	2-2'-azobis(2-amidinopropane) dihydrochloride
ABTS	2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt
ABTS <sup>•+</sup>	ABTS radical cation
ABTSH <sup>+</sup>	reduced ABTS <sup>•+</sup>
AH	antioxidant (with proton attached)
ANI	aniline
APS	ammonium persulfate
AUC	under the ORAC fluorescence decay curve
B	benzenoid
BHT	butylated hydroxytoluene
CP	conducting polymer
CPS	counts per second
CV	cyclic voltammetry
DBSA	dodecylbenzenesulfonic acid
DHA	docosahexaenoic acid
DMSO	dimethyl sulfoxide
DPPH	2,2'-diphenyl-1-picrylhydrazyl
DPPH•	DPPH free radical

e <sup>-</sup>	electron
EC	ethyl cellulose
EDOT	3,4-ethylenedioxythiophene
EDXS	energy-dispersive X-ray spectrometry
EPA	eicosapentaenoic acid
ESR	electron spin resonance spectroscopy
ET	electron transfer
eV	electron volt
FH	fluorescein (with proton attached)
FTIR	fourier transformation infrared spectroscopy
GC	gas chromatography
H <sup>+</sup>	proton
HAT	hydrogen atom transfer
HIPEF	high-intensity pulsed electric fields
HX-Fe <sup>+3</sup>	metmyoglobin
ITO	Indium tin oxide electrode
LH	lipid (with proton attached)
mS	milli-Siemens
mT	milli-Tesla
ORAC	oxygen radical absorbance capacity
β-PE	β-phycoerythrin
PANI	polyaniline
PANI1.5	PANI prepared with a ratio of APS to ANI of 1.5 to 1

PANI(OX)EC	PANI EC composite prepared by polymerizing aniline in a EC matrix with presence of APS oxidant
PE	polyethylene
PEDOT	poly (3,4-ethylenedioxythiophene)
PEDOT1.0	PEDOT prepared with a ratio of APS to EDOT of 1.0 to 1
PNMPy	polyN-methylpyrrole
PPy	polypyrrole
PPy0.5	PPy prepared with a ratio of APS to Py of 0.5 to 1
PPya	PPy made with addition of acid
PV	peroxide value
Py	pyrrole
Q	quinoid
RedPEDOT1.0	PEDOT1.0 reduced with hydrazine
RedPANI1.5	PANI1.5 reduced with hydrazine
RedPPy0.5	PPy0.5 reduced with hydrazine
R <sub>2</sub> N <sub>2</sub>	AAPH
RH	organic substrate (with proton attached)
ROO•	peroxyl radicals
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
V	volt
X•	oxidizing agent
•X-[Fe <sup>+4</sup> = O]	ferrylmyoglobin

XPS

X-Ray photoelectron spectroscopy