CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

In this work, N-phthaloylchitosan was successfully synthesized and its structure has been verified by FTIR and ^{1}H NMR spectroscopy. Three main peaks at 1772, 1708 and 719 cm^{-1}, assigned to phthalimido groups and aromatic groups, respectively are present in the FTIR spectrum. In the ^{1}H NMR spectrum, two sets of peaks appeared at 2.0 to 5.0 ppm and 7.0 to 8.0 ppm assigned to proton from backbone chitosan and aromatic groups, respectively. FTIR and ^{1}H NMR results verified that N-phthaloylation and small extension of O-pthaloylation had taken place onto chitosan. The crystallinity of the modified chitosan was examined by XRD diffractogram. PhCh is observed to be more amorphous in nature compared to pure chitosan as two peaks at $2\theta = 15.1^o$ and 20.6^o from pure chitosan diffractogram merge into a one broad peak at 21.7^o at 2θ. PhCh was found to be completely soluble in DMF, DMSO, DMAc and pyridine. However, from the estimation of solubility parameter, PhCh with solubility parameter, σ_{pol} of 24.2 closely matched with DMF, with the solubilibity parameter of solvent, $\sigma_{sol} = 24.9$.

PhCh was used as a host for polymer electrolytes. Films of PhCh were prepared by solvent casting technique. DMF was chosen as the solvent with addition of LiI as the doping salt. Comparison of FTIR spectra between PhCh in powder and film form has been made (*Figure 4.6*). Spectrum of PhCh film showed peak at 1650 cm^{-1} assigned to the amide group which might be due to the ring-opening of phthalimido group to give an amide and a carboxylic acid group. The ionic conductivity of pure PhCh film was found to be 1.87 x 10^{-}

^{10} S cm^{-1}. The conductivity was increased to the maximum of 1.88 x 10^{-4} S cm^{-1} after addition of 50 wt.% of LiI into the PhCh-LiI system at room temperature.

The increment of conductivity is attributed to the increase in the number of ions in PhCh-LiI system due to dissociation of salt. Besides that, the increase of amorphousness of the polymer electrolyte after more LiI salt was added also contributed to the increase of ionic conductivity. The more amorphous the sample, the higher is the ionic conductivity. Temperature is also one of the factors that assist the increment of ionic conduction by further increase the degree of salt dissociation and ionic mobility. Relationship between conductivity and temperature of PhCh-LiI system obeys the Arrhenius Law. The activation energy obtained was decreased with the addition of salt parallel to the conductivity results. The faster the movement of ions results in a decrease of relaxation time. The relaxation time that is estimated by taking reciprocal of the peak frequency from loss tangent-frequency plot also agrees the conductivity increase with addition of salt and temperature.

Interaction PhCh with LiI salt to form PhCh-salt complexes can be observed from the FTIR studies. The phthalimido band at 1772 cm^{-1} shifted to higher wavenumbers. The interaction leads to the transformation of PhCh forming amide and carboxylic acid groups. The breakage of the phthalimido group is confirmed by the presence of amide band at 1654 cm^{-1} and the band shifted to 1649 cm^{-1} after addition of 50 wt.% of LiI.

The most conducting PhCh-LiI polymer electrolyte has been applied in dye-sensitized solar cell by using two natural dyes extracted from black rice and red cabbage. The most efficient DSSC using dye extracted from black rice performed by pH 2 gave V_{OC} = 0.32 V, J_{SC} = 1.24 mA cm^{-2} and FF = 0.44. While that using dye extracted from red cabbage performed at pH 1 gave V_{OC} = 0.28 V, J_{SC} = 0.32 mA cm^{-2}, FF = 0.44 and η = 0.03. Comparison of both natural dyes at pH 1 following the work of Buraidah et. al [119] shows that black rice is a better sensitizer compared to red cabbage since it showed higher *FF* or and η. This is due to the difference in chemical structure of the dye extract.

Further work should be carried out to improve the performance of PhCh based polymer electrolytes in the devices. An interesting approach to improve the ionic conductivity at ambient conditions is addition of plasticizer. Adding plasticizer, a small molecules or oligomers with coordinating/ solvating ability to the polymer, is an interesting alternative to overcome the limitation inherent in a mixture of only polymer and salt. By introducing plasticizer into the polymer electrolyte, the matrix will become more liquid, thus able to:

- Decrease the glass transition temperature, T_g of the polymer electrolyte.
- Make polymer electrolyte more flexible.
- Reduce the local viscosity and thereby facilitate the mobility and conductivity
- Decrease the ductility and improve its impact resistance.
- Reduce the crystallinity as this assists the increasing of the conductivity.

Plasticizer used must meet all these criteria [120]:

- Dielectric constant should be higher than that of the polymer used
- Good miscibility with polymer electrolytes
- Low volatility
- Stability towards electrode materials
- Low freezing temperature
- High boiling temperature

Some of the plasticizers that have been introduced into the polymer electrolytes are shown in *Table 5.1*. Combination of DMA and DEC into PEO and PMMA assisted the conductivity to increase to 2 and 4 magnitudes, respectively. EC, PC and the combination of both plasticizers are also some of the popular plasticizers that have been frequently used in polymer electrolytes. Enhancement of the conductivity values can be observed by adding EC and/or PC into PAN, PMMA, PEO, diglyme, natural rubber and chitosan doped with lithium salts.

Table 5.1: Variations of plasticizers introduced in polymer electrolytes

Platicizer	Polymer	Salts	σ before adding plasticizer, S cm^{-1}	σ after adding plasticizer, S cm^{-1}	References
Dimethylacetamide (DMA) & diethylcarbonate (DEC)	PEO	NH_4F	10^{-6}	10^{-4}	Kumar et al. (2002)
	PMMA	$NH_4CF_3SO_3$	10^{-6}	10^{-2}	Kumar et. al (2005)
Polyethylene glycol, PEG_{200}	PEO	NaI	10^{-8}	10^{-7}	Pradan et. al (2009)
Ethylene carbonate (EC) & propylene carbonate (PC)	PEO	$LiCF_3SO_3$	10^{-4} at 120 °C	Increased 3-4 order	Chintapalli et al. (1996)
			10^{-5}	10^{-4}	Bandara et al. (1998)
	PAN-PMMA	$LiClO_4$	-	10^{-3}	Ostrovskii et al. (1998)
PC	PAN	$LiCF_3SO_3$	-	-	Starkey et al. (1997)
	Diglyme	$LiCF_3SO_3$	-	-	Huang et al. (1995)
EC	Natural rubber	$LiCF_3SO_3$	-	-	Kumutha et al. (2005)
	Chitosan	$LiCF_3SO_3$	-	-	Osman et al. (2003)

Currently project deals with development of the polymer electrolyte through phthaloylation and its application in DSSC. For further works, this modified chitosan polymer electrolyte can be investigated for its use in other devices such as lithium-ion battery and capacitor. This is because lithium-ion battery has been commercialized in small portable devices such as camcorders and cell phones [121]. In addition, lithium ion battery fulfills the current demand features for reduced-size batteries with long durability, high safety and low aggression potential to the environment when discarded [122].