PHASE BEHAVIOUR AND MORPHOLOGY IN BLENDS OF POLYETHER AND POLYACRYLATE WITH THE ADDITION OF LITHIUM SALT



RESEARCH MANAGEMENT INSTITUTE (RMI) UNIVERSITI TEKNOLOGI MARA 40450 SHAH ALAM, SELANGOR MALAYSIA

BY :

ASSOC. PROF. Dr. SIM LAI HAR

HEAD OF PROJECT

ASSOC. PROF. DR. CHAN CHIN HAN PROF. HANS-WERNER KAMMER

TEAM MEMBERS

AMIRAH BINTI HASHIFUDIN POSTGRADUATE MEMBER

OCTOBER 2013

i

Contents

1.	Letter of Report Submission					
2.	Letter Of Offer (Research Grant)					
3.	Acknowledgements					
4.	Enhanced Research Title and Objectives					
5.	Report					
	5.1	Proposed Executive Summary	4			
	5.2	Enhanced Executive Summary	5			
	5.3	Introduction	5			
	5.4	Brief Literature Review	7			
	5.5	Methodology	8			
	5.6	Result and Discussion	10			
	5.7	Conclusion and Recommendation	15			
	5.8	References/Bibliography	15			
6.	Research Outcomes					
7.	Appendix					

2. Letter of Offer (Research Grant)





Surat Kami Tarikh : 600-RMI/ST/DANA 5/3/Dst (427 /2011) | Oktober 2011

Profesor Madya Dr Sim Lai Har Fakulti Sains Gunaan Universiti Teknologi MARA 40450 Shah Alam

Y. Brs. Profesor/Tuan/Puan

KELULUSAN PERMOHONAN DANA KECEMERLANGAN 10/2011

Tajuk Projek		The Phase Behaviour and Morphology in Blends of Polyether and Polyacrylate with the Addition of lithium salt
Kod Projek		600-RMI/ST/DANA 5/3/Dst (427 /2011)
Kategori Projek		Kategori G (2011)
Tempoh		01 Oktober 2011 – 30 September 2013 (24 bulan)
Jumlah Peruntukan		RM 8,000.00
Ketua Projek	:	Profesor Madya Dr Sim Lai Har

Dengan hormatnya perkara di atas adalah dirujuk

2 Sukacita dimaklumkan pihak Universiti telah meluluskan cadangan penyelidikan Y Brs Profesor/tuan/puan untuk membiayai projek penyelidikan di bawah Dana Kecemerlangan UiTM

3 Bagi pihak Universiti kami mengucapkan tahniah kepada Y. Brs. Profesor/tuan/puan kerana kejayaan ini dan seterusnya diharapkan berjaya menyiapkan projek ini dengan cemerlang.

4. Peruntukan kewangan akan disalurkan melalui tiga (3) peringkat berdasarkan kepada laporan kemajuan serta kewangan yang mencapai perbelanjaan lebih kurang 50% dari peruntukan yang diterima.

Peringkat Pertama	20%
Peringkat Kedua	40%
Peringkat Ketiga	40%

5. Untuk tujuan mengemaskini, pihak Y. Brs. Profesor/tuan/puan adalah diminta untuk melengkapkan semula kertas cadangan penyelidikan sekiranya perlu, mengisi borang setuju terima projek penyelidikan dan menyusun perancangan semula bajet yang baru seperti yang diluluskan. Sila lihat lampiran bagi tatacara tambahan untuk pengurusan projek.

Sekian, harap maklum

"SELAMAT MENJALANKAN PENYELIDIKAN DENGAN JAYANYA"

Yang benar

PROFESOR DR ABU BAKAR ABDUL MAJEED Penolong Naib Canselor (Penyelidikan)

tan yan s _{ag} bern tal sin "sin nat y n _{ad} n tan nat		Sanata nagagan kangkan dalap sa Mana nagagan Sanda Sanata San Bagan gapan Sanda Jagan J Sanata dalap dari		Penalong Pentadbiran 1532 Foot Kewangan Zon P	$\mathcal{C} > 3 \leq 5.544 \mathcal{O} = 1.541 $	
(HALL)	Research Management Institute (RM http://www.rmi.uitm.ed	l) Universiti Teknologi MARA u . <i>m y</i>	., 40450 Shah Alam,			

properties while the hierarchical morphology of this multiphase blend can retained. With the desired morphology, the salt shall dissolve in the amorphous phase of the blend which forms the percolating pathway for fast cation movement.

The objectives of this study are (i) to prepare the compatible PEO/polyacrylate blend through the appropriate choice of polyacrylate and the optimization of processing conditions (ii) to characterize the thermal stability, conductivity, morphology, mechanical properties and the interactions between the two constituents. Minimum one master thesis in UiTM will be produced. Oral presentations in local conferences and a minimum of one publication in international refereed journal (Scopus indexed) are expected.

5.2 Enhanced Executive Summary

(Abstract of the research) – 1 page only

Solution casting technique is employed to prepare the poly(ethylene oxide) (PEO)/ polyacrylate (PAc) blends. Thermal behaviour and ionic conductivity of the PEO/PAc and PEO/PAc blends added with LiClO₄ were investigated using differential scanning calorimetry (DSC) and impedance spectroscopy (IS), respectively. Observations of a single composition-dependent glass transition temperature (T_q) which agrees closely with that calculated using the Fox equation, coupled with successive suppression of the melting temperature (T_m) and crystallinity of PEO with ascending PAc content, affirm the miscibility of the two constituents in the blend. The conductivity of salt-free PEO is enhanced with the addition of \leq 25 wt% of PAc due to the reduced crystallinity of PEO in the blend. The T_g values of the blend at all compositions under study increase with the addition of LiClO₄. Ionic conductivity of the salt-added blend increases with increasing salt concentration. The amorphous phase of PEO forms the percolating pathway in the homogeneous PEO/PAc/LiClO₄ blends as blends with PEO content \geq 25 wt% (PEO/PAc 75/25 blend) records slightly higher σ values at concentration of $LiClO_4$ (Y) > 0.02. Enhancement in ionic conductivity in the blend is probably the result of increase charge carrier density and ionic dynamic of the PEO macromolecular chain.

5.3 Introduction

1 to 2 pages only

The rapid development in advanced electrochemical and micro-ionic devices has attracted extensive research on polymer electrolytes, with the desire of applying these electrolytes in new generation high performance rechargeable batteries¹⁻⁵. Over the last three decades, poly(ethylene oxide) (PEO) remained to be the focus in most of the researches on solid state batteries because of its strong solvating capability of wide variety of inorganic salt and its low glass transition temperature $(T_g)^{6-9}$.

It is well documented that the amorphous phase of PEO forms the percolating pathway for fast ion transport in PEO-salt system¹⁰⁻¹¹. Glass transition temperature results obtained in the previous studies¹²⁻¹⁴ have verified that no isotropic dispersion of Li⁺ ion in different phases of a blend is demonstrated for both the immiscible blends of PEO/epoxidized natural rubber (ENR) and PEO/polyacrylate (PAc) with the addition of LiClO₄, instead, the Li⁺ ion has a higher solubility in the amorphous phase of PEO as compared to ENR or PAc, respectively. Besides, LiClO₄ is found to be more soluble in the amorphous PAc than in ENR when equal amount of the salt is added to the immiscible PEO/ENR and PEO/PAc systems of the same blend composition¹²⁻¹⁴. Furthermore, with the addition of salt, the $T_{g}s$ of PAc in the PEO/PAc/LiClO₄ blend are raised to the range of 26 - 42 °C at which conductivity of the blend is measured. Therefore, higher charge density in the PEO amorphous phase of the heterogeneous PEO/ENR/LiClO₄ blend accounts for the higher ionic conductivity of the blend as compared to that in the PEO/LiClO₄ system. On the contrary, due to a reasonable amount of the salt being locked in the glassy PAc, the reduction in charge density in the PEO amorphous phase for the immiscible PEO/PAc/LiClO₄ blend causes the conductivity of the blend to be lower than that of the PEO/LiClO₄ system¹⁵.

In the blend preparation of PEO/PAc and PEO/PAc/LiClO₄ electrolyte films described in the previous study¹⁵, solution cast free standing film was dried in a vacuum oven for 48 h at 50 °C. Calorimetric analysis using differential scanning calorimetry (DSC) shows that both the salt-free and salt-added blend systems are immiscible marked by the presence of two T_g s and a relatively constant PEO crystallinity (X^*) with increasing PAc content. However, miscible PEO/PAc and PEO/PAc/LiClO₄ blends are obtained in the present work when the solution cast free standing film was heated at 80 °C (above the melting point of PEO) for 2 h under nitrogen atmosphere before vacuum dried for another 24 h at 50 °C.

A brief description of the thermal treatment applied in the preparation of the homogeneous PEO/PAc blend with and without the addition of the inorganic salt, LiClO₄ is presented in the present study. Miscibility of the two polymer components of the blend was investigated by thermal analysis using differential scanning calorimetry