POLYETHYLENE OXIDE-MCM-41 AND POLYANILINE-MCM-41 NANOCOMPOSITES: PHYSICOCHEMICAL AND CONDUCTING PROPERTIES

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Dedicated to my beloved mother, family and…especially for my fiancé

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ABSTRACT

One of the exciting developments in material science today is the design and synthesis of polymer nanocomposites (PNC) containing electrically-conductive polymer and mesoporous MCM-41 that possess novel properties not exhibited by the individual organic and inorganic materials. The physicochemical and conducting properties of two types of PNC namely, PEO/Li-MCM-41 and PANI/MCM-41 prepared by melt and solution intercalation and *in situ* polymerisation methods have been investigated in this thesis. The aim was to obtain a more detailed understanding of how the combination of polymers with the mesoporous MCM-41 is related to the conducting properties of the PNC. Before PEO and PANI are combined with MCM-41, several modifications of MCM-41 have been done including ion exchange of MCM-41 with lithium chloride, silylation of MCM-41 with trimethylchlorosilane (TMCS) and functionalization of MCM-41 with sulfonic acid. The PNC obtained was characterized by X-ray diffraction (XRD), infrared (IR) spectroscopy, thermogravimetric analysis and chemical analysis, followed by ^{27}Al, ^{7}Li and ^{13}C/CP MAS NMR spectroscopy. It is confirmed that the structure of MCM-41 remains intact after combining with the polymers. The results from the conductivity study have proven that the PNC possesses electrical properties. It is revealed that the conductivity of PANI/MCM-41 is very much higher than PEO/Li-MCM-41 since PANI is a conducting polymer whereas PEO is a polymer electrolyte. The combination of PEO and MCM-41 was expected to increase the conductivity of PEO/Li-MCM-41 by intercalation of PEO inside the pores of MCM-41. However, it is demonstrated that unmodified Li-MCM-41 exhibits conductivity in the same order of magnitude as the PEO/Li-MCM-41. The NMR results suggested that the interfacial interactions occurring between the PEO and Li-Al-MCM-41 is insufficient to improve the conductivity of the PEO/Li-MCM-41 nanocomposite. On the other hand, PANI/MCM-41 nanocomposite shows an increase in thermal stability of conductivity compared to PANI, although its conductivity was lower in the presence of MCM-41.

ABSTRAK

Antara pembangunan yang menarik dalam bidang sains bahan masa kini ialah rekabentuk dan sintesis nanokomposit polimer (PNC) yang mengandungi polimer mengkonduksi elektrik dan bahan mesoliang MCM-41 yang mempunyai sifat khas yang tidak dapat dimiliki bahan asal organik dan tak organik secara individu. Sifat fizikokimia dan kekonduksian bagi dua jenis PNC seperti PEO/Li-MCM-41 dan PANI/MCM-41 yang telah disintesis menggunakan teknik interkalasi leburan dan larutan serta pempolimeran *in situ* telah dikaji dalam tesis ini. Matlamat kajian ini adalah untuk memahami secara mendalam kombinasi antara polimer dan bahan mesoliang MCM-41 dan hubungannya dengan sifat kekonduksian. Sebelum PEO dan PANI digabungkan dengan MCM-41, beberapa modifikasi telah dilakukan terhadap MCM-41 seperti penukaran ion dengan litium klorida, sililasi dengan trimetilklorosilana (TMCS) dan pemfungsian dengan asid sulfonik. PNC telah dicirikan dengan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah (IR), analisis termogravimetri dan analisis kimia, diikuti dengan spektroskopi ^{27}Al, ^{7}Li dan ^{13}C/CP MAS NMR. Struktur MCM-41 telah dipastikan tidak mengalami perubahan selepas bergabung dengan polimer tersebut. Kajian kekonduksian telah menunjukkan bahawa PNC memiliki sifat kekonduksian elektrik. Kekonduksian PANI/MCM-41 adalah jauh lebih tinggi berbanding PEO/MCM-41 disebabkan PANI adalah polimer mengkonduksi manakala PEO adalah polimer elektrolit. Kombinasi PEO dan MCM-41 secara interkalasi PEO di dalam liang MCM-41 dijangkakan dapat meningkatkan kekonduksian nanokomposit polimer PEO/Li-MCM-41. Sebaliknya, dalam kajian ini Li-MCM-41 tanpa diubahsuai menunjukkan kekonduksian yang sama seperti PEO/Li-MCM-41. Data NMR menunjukkan interaksi permukaan berlaku di antara PEO dan Li-MCM-41 tetapi ianya tidak mencukupi untuk meningkatkan kekonduksian PEO/Li-MCM-41. Selain daripada itu, nanokomposit PANI/MCM-41 menunjukkan kestabilan terma kekonduksian yang meningkat berbanding PANI, begitu pun, kekonduksiannya menjadi lebih rendah dengan kehadiran MCM-41.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

2θ	-	Bragg Angle
BET	-	Brunnauer, Emmett and Teller
Cu K_α	-	X-ray diffraction from Copper K energy levels
FTIR	-	Fourier Transform Infrared Spectroscopy
KBr	-	Potassium Bromide
LiCl	-	Lithium Chloride
MAS NMR	-	Magic-Angle-Spinning Nuclear Magnetic Resonance
MPTS	-	Mercaptopropyltrimethoxysilane
nm	-	Nanometer
PANI	-	Polyaniline
PANI.DS	-	Polyaniline Doped Dodecylsulfonic Acid
PANI.HCl	-	Polyaniline Doped Hydrochloric Acid
PEO	-	Polyethylene Oxide
PMS	-	PANI/Si-MCM-41SO_3H Nanocomposites
PNC	-	Polymer Nanocomposites
PS	-	PANI.DS
SDS	-	Sodium Dodecylsulfate
SiO_2/Al_2O_3	-	Silica to Alumina Ratio
TGA	-	Thermogravimetric Analysis
TMCS	-	Trimethylchlorosilane
UV/Vis	-	Ultraviolet/Visible
XRD	-	X-ray Diffraction

LIST OF APPENDICES

CHAPTER 1

GENERAL INTRODUCTION

1.1 Research Background

Composites are generally defined as materials which are made by physically combining two or more existing materials to produce a multiphase system. The phase of the composites formed might differ from the starting material, depending on chemical interaction occurred [1]. There are many types of composites such as conventional microcomposites and nanocomposites. Nanocomposites are composites in which the components are combined in at least one dimension either the length, width or thickness in the size ranges 1-100 nm. Differing from the conventional microcomposite, nanocomposite is combination of two phases in which one of the materials has at least one dimension in the nanometer range (10^{-9} m) and gives possibility to synthesize nanostructured materials showing improved chemical and physical properties which are not exhibited as individual properties.

Recently, polymer-inorganic nanocomposite received wide attention in the field of materials science both in industrial and academia [2,3]. The most interesting is to synthesize intercalated polymers in inorganic materials such as layered silicates, mesoporous materials and zeolites. Two major findings have stimulated the revival of interest in these materials; first, the report from Toyota research group of a Nylon-6/montmorillonite (MMT), for which very small amounts of layered silicate loading resulted in pronounced improvements of thermal and mechanical properties [2]; and second the observation from Vaia *et al.,* that it is possible to melt-mix polymer with layered silicates without use of organic solvent [3]. Today, efforts are being conducted globally, using almost all types of polymer matrices.

In general, organic polymer and inorganic materials have contrasting properties. Organic polymers are hydrophobic, flexible, tough, and are easy to process, but they can also relatively easily damaged either chemically or mechanically. In contrast, the inorganic materials are mostly hydrophilic, typically much harder and have good chemical stability but are also brittle and difficult to process. Many properties including strength, conductivity and chemical stability are dramatically improved after combining the polymer with inorganic materials [1,2,3]. These examples clearly illustrate some of the characteristic of polymer-inorganic nanocomposites.

There are many approaches that have been used by researchers to synthesize intercalated polymer-inorganic composites. The most important aspect in the preparation of these composites is to increase the interaction between polymer and inorganic materials. Different techniques have been used to synthesize intercalated polymer-inorganic composites such as melt intercalation technique, solution intercalation technique and *in situ* polymerization [2]. Besides that, in order to prepare homogeneous and intercalated composites of organic polymer and inorganic materials, many researchers have attempted to change chemical properties of these materials in order to increase similarity between them. For example, hydrophobicity of inorganic materials has been increased in order to make organic polymers easier to intercalate in the inorganic materials.

1.2 Research Objectives

In this thesis we wish to investigate the physicochemical properties of electrically-conductive polymer-mesoporous MCM-41 nanocomposite. MCM-41 was chosen as the inorganic host because of its extremely high surface area which is more than 1000 m^2/g and large pore size with the diameter between 15 and 100 Å.

Polyethylene oxide (PEO), an electrolyte polymer and polyaniline (PANI), a conducting polymer have been used as source of polymers.

In this study, polymer-mesoporous material nanocomposite is synthesized by means of intercalation techniques. It is important to note that there are two possible structures of nanocomposites which consist of intercalated nanocomposites and conventional nanocomposites. Polymer chain is intercalated in the pores of MCM-41 in intercalated nanocomposites, meanwhile, the polymers are located on the external surface of MCM-41 in conventional nanocomposites. For a maximum interfacial interaction between polymer and mesoporous MCM-41, conventional nanocomposites should be minimized. One expects that increase interfacial interaction efficiency can increase the conductivity properties of the nanocomposite. However before this objective can be achieved, basic knowledge about that structure-property of the nanocomposite is required. Only with this knowledge, polymer-MCM-41 can be designed in order to obtain products with the desired properties. This defines the objective of the present investigations:

“The primary aim of this investigation is to obtain a more detailed understanding of how the combination of polymers with mesoporous MCM-41 is related to the conducting properties.”

1.3 Scope of Thesis

This thesis deals with the study of structure-conducting properties of the combination of polyethylene oxide (PEO) and polyaniline (PANI) with mesoporous MCM-41 prepared by melt and solution intercalation techniques. These two types of polymers have attracted world-wide academic and industrial attention during the last decade. Typically, these materials show promising performances in the practical applications of electrically-conductive polymer composites, i.e. for a solid polymer fuel cell. Despite the extensive research in this field, various aspects are not clarified yet. For instance, the interfacial interaction of polymer-mesoporous silica is much debated as well as the various described preparation procedures. Chapter 2 concerns with the extensive characterization and conducting properties of various kinds of PEO/Li-MCM-41 nanocomposites prepared by melt and solution intercalation techniques. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), solid state MAS NMR and conductivity measurement were used to characterize these polymer nanocomposites (PNC) in an attempt to correlate the structure and conductivity. In Chapter 3, PANI/MCM-41 nanocomposites have been prepared by *in situ* polymerization technique. Thermal stability of conductivity of the polymer nanocomposites (PNC) was studied in order to know the effect of MCM-41 in PANI/MCM-41 nanocomposites. Finally, concluding remarks will be given in Chapter 4.

MCM-41, as analyzed by solid-state NMR, is relatively high. This causes the retardation of the mobility of Li^+ ions in the PNC. It can be concluded that the interactions that occur in the nanocomposites are insufficient to improve conductivity of the PEO/Li-MCM-41 nanocomposites.

PANI/MCM-41 nanocomposite was obtained by *in situ* polymerization method. Before the polymerization, MCM-41 was functionalized with sulfonic acid. It is revealed that although conductivity measurement shows that conductivity of PANI was reduced after addition of MCM-41, its thermal stability of conductivity was significantly enhanced. As a global guide for future actions, this work opens new perspectives for the use of PANI/MCM-41 nanocomposite as a conducting material at high temperature.

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