THE EFFECT OF SILICON DIOXIDE ON THE ELECTRICAL CONDUCTIVITY OF POLYPYRROLE/ POLY (VINYL CHLORIDE) BLENDS AS A CONDUCTING POLYMER FOR THE IONIC SOLUTIONS DETECTOR

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KESAN SILIKON DIOKSIDA TERHADAP KEKONDUKSIN ELEKTRIK ADUNAN POLIPIROL / POLI (VINIL KLORIDA) SEBAGAI POLIMER KEBERAURAN UNTUK MENGEJAN LARUTAN BERIONIK

ABSTRAK

Polipirol/poli(vinil klorida)-silikon dioksida komposit polimer keberaliran telah dikaji sebagai polimer keberaliran untuk mengesan larutan berionik. Komposit ini disediakan dari campuran polipirrol berisi hitam karbon dan kandungan silikon oksida yang berbeza. Campuran komposit dilarutkan dengan 1-metil2-pirolidinona dan kemudian dipanaskan pada suhu didih untuk sehingga berlaku pempolimeran. Adunan PPy/SiO_2 dicampurkan dengan gel PVC yang berfungsi untuk meningkatkan rekatan di permukaan kepingan PCB. Komposit polimer keberaliran telah dianalis dengan spektroskopi inframerah tranformasi (FTIR), Mikroskop pengimbas elektron (SEM), kolometri pengimbasan perbezaan (DSC) dan pembelauan sinar-X (XRD). Hasil menunjukkan keberaliran elektrik meningkat dengan meningkatnya kandungan silikon oksida dalam komposit. Mikrograf SEM adunan PPy/PVC menunjukkan ia sesuai sebagai alat pengesan untuk semua larutan yang diuji. Kalium klorat menunjukkan keberaliran elektrik yang tinggi dibandingkan terhadap larutan natrium klorida dan ammonium hidroksida. Interaksi antara molekul di antara fasa PPy/PVC dengan silikon oksida sangat jelas ditunjukkan oleh analisa FTIR.

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ABSTRACT

Polypyrrole/poly (vinyl chloride)-silicon dioxide conducting polymer composites has been investigated as conducting polymer for ionic solutions detector. These composites were prepared by mixing polypyrrole doped with carbon black and different of silicon dioxide loading as variable. The mixture was dissolved in 1-methyl-2-pyrrolidinone and then heated under boiling point to obtain conductive polymer solution. Poly (vinyl chloride) carboxylated was dissolved in Tetrahydrofuran (THF) and heated until it becomes gel. The PPy/SiO_2 blend was mixed with PVC gel which was used as binder to improve the adhesion of the sensing material on sensor electrodes. PPy/PVC-SiO_2 conductive polymer composites samples had been characterized by FTIR, DSC and XRD analysis. After the dropping of the samples to surface of PCB board of sensors, they dried into oven and then connected to precision multimeter to measure their resistance when applied to the solutions. The results showed the electrical conductivity increased with increasing SiO_2 content in composite. The PPy/PVC blends under SEM micrographs and XRD characterizations exhibited the agglomeration and intercalation between PPy and PVC/SiO_2 which supported the electrical conductivity result. The Potassium chlorate exhibited highest electrical conductivity compared to other solutions. The intermolecular interaction between PPy/PVC with SiO_2 is evidenced from FTIR analysis.

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LIST OF SYMBOLS, ABBREVIATIONS OR NUMENCLATURE

A	The average area of sensing device
Å	Angstrom
ASTM	American Standard Testing Material
°C	Degree Celsius
CB	Carbon Black
CPC	Conducting polymer composite
CPs	Conducting Polymers
DSC	Differential Scanning Calorimetry
E_g	Band Gap Energy
eV	Electron volt
$FeCl_3$	Iron (III) chloride
FTIR	Fourier Trans Infrared Spectroscopy
g	Gram
HOMO	Highest Occupied Molecular Orbital
ICP	Intrinsically conducting polymer
J	Joule
$KClO_3$	Potassium chlorate
LUMO	Lowest Unoccupied Molecular Orbital
$MgCl_2$	Magnesium chloride
MP	1-Methyl-2-pyrrolidone
mL	Millilitres
NaCl	Natrium chloride

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NH_4OH	Ammonium hydroxide
PPy	Polypyrrole
PVC	Polyvinyl chloride
R	The resistance of sensing device
S/cm	Siemens per centimeter
SEM	Scanning Electron Microscope
SiO_2	Silicon Dioxide
T	The thickness of sensing device
T_g	Glass transition
THF	Tetrahydrofuran
T_m	Melting point
XRD	X-ray Diffraction
V/v	Volume/volume
σ	Electrical conductivity of sensing device
Ω	Ohm (unit of resistance)
ΔH	Enthalpy of fusion
2θ	Diffraction angle

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CHAPTER 1

INTRODUCTION

1.1 Background

Currently, conducting polymers have been the subject of great interest to chemists and physicists. Polypyrrole (PPy) has been one of the most studied polymers because of its physical and electrical properties that have led to several applications such as solid state devices and electronics. However, its poor mechanical properties, e.g., brittleness, and low level of processability constitute major obstacles to its extensive application. To improve the structural and physical properties, several attempts have been made to prepare blends or composite materials containing PPy (Migahed et al., 2004).

The weakness of polypyrrole can be shown by low elongation at break and brittleness points and thus cannot be fabricated or molded into a desirable form. These properties can severely restrict the applications of such polymers. The mechanical properties can be further enhanced by the forming of composite materials of the conducting polymer by incorporating it into a polymeric m atrix having superior mechanical properties. Several composites of PPy with different chemicals such as polyvinyl chloride PVC, poly(acrylonitrile)PAN,polyether-polyester, polyurethane, nylon-6,6, Nafion ,and cellophane have been reported. These composites have been produced using different routes such as chemical, electrochemical, vapor deposition, interface technique and plasma polymerization. The conductivity of such composites has

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been found to be comparable to that of pure PPy whereas its mechanical properties are further improved (Narendfu et al., 1999).

Radhakrishnan and Deshpande, (2002) reported that the conducting polymers are often infusible and insoluble. Consequently, immobilization by entrapment of specific molecules that are capable of substrate recognition can be carried out mainly during polymerisation process. However, this growing reaction added to the entrance of negatively charge species (sometimes positive ones) makes it possible to entrap various moieties easily in a one step process, with the further advantages of intrinsic porosity and electronic accessibility.

Filler morphology influence on the percolation threshold has been studied. Lux, (1993) reported that small particles can lead to a lower percolation threshold this was however not confirmed by the present studies. Conductive PPy exhibiting larger particle sizes can further lead to blends which then show the lowest percolation threshold. The smaller particle size increases the changed tendency to agglomeration. Therefore, in the blends prepared with the PPy exhibiting the smallest particles size, *i.e.*, PPy synthesized by dispersion polymerization, a percentage of the small PPy particles formed subsequently go on to form agglomerates. These large agglomerates then become the conductive entities and subsequently, high PPy ratio is required to form an infinite cluster which then further ensures the electrical conduction of the blend (Cassugnol et al., 1999). The PPy that is prepared via the process of suspension polymerization is the most convenient filler available to make the epoxy matrix electrically conductive, however larger agglomerates present in the PPy/epoxy matrix can act as the initiating flaws and this in turn may give rise to poor mechanical properties.

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The thermal, mechanical and electrochemical behavior properties of poly (vinyl chloride)/ polypyrrole (PVC/PPy) blends were further studied by Mano, et al. (1996) and Xu, et al. (2007). From the study it was found that high-strength and highly-conductive polymer films could be obtained based on the application of the electrochemical methods. The composite was then further characterized by the following processes: Attenuated total reflectance FTIR spectroscopy, differential scanning calorimetry and dynamic mechanical analysis. Infrared reflectance spectra further suggested that the polymerization could occur preferentially on the matrix surface producing sandwich-type structures. The mechanical, thermal and conducting behavior showed a dependence on the initial concentration of Iron (III) chloride in the matrix and the duration of exposure to pyrrole vapor In addition, the stress-strain behavior of PVC/PPy blends that were obtained from PVC/ Iron (III) chloride matrices and exposed to pyrrole for a duration of 2 h and 6 h further indicated the important changing trend that the yield stress and Young's modulus of film/coating decreased as the concentration of Iron (III) chloride increased from 1% to 35%.

Conducting composites that were synthesized by the oxidation polymerization of pyrrole inter penetrated in ethylene-vinyl alcohol copolymer and the oxidant used was Iron (III) chloride. Migahed et al. (2004) reported that the conductivity of composite films could reach up to 1 S/cm and could be further controlled by varying the polypyrrole (PPy) variable in the composite. The activation energy, Ea, of the conductivity was further evaluated using the Arrhenius relationship in the low temperature region. It was found that the values of the activation energy decreases as the PPy content increases, which further suggests the formation of more polarons. The conductivity was analyzed by using the variable range hopping model and the optimal

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results have been achieved for a one dimensional model for charge transport in the present conducting composites. The electrically conducting polymer composite films have been further characterized by the following processes: scanning electron microscopy, ultraviolet/visible and infrared spectroscopy and wide angle X-ray diffraction spectroscopy. The morphology changes of the composite films could be attributed to the synthesis conditions.

Zhang et al. (2007) studied the further effects of silica concentration on the electrical conductivity of carbon black–silica/epoxy nanocomposites provided deeper understanding for its nature. It was found that with increasing content of silica, CB particles were optimally dispersed, which then enhances the generation of a conductive network. Compared with the nanocomposites containing no silica, the conductivity of the nanocomposites containing CB particles increased with an increasing volume fraction of silica to reach a maximum value at a ratio of 0.6:1.0 (SiO_2:CB).

The electrical conductivity of the prepared polypyrrole-polyethylene glycol (PPy-PEG) conducting polymer composite films was measured at room temperature by a four-point probe technique, taking the average value of several readings at various points of the composite films. The highest conductivity of PPy-PEG composite films were measured at room temperature and were found to be 61.3 S/cm for the film prepared from 0.2 M pyrrole with 0.2 % PEG and 0.1 M *p*-toluene sulfonate (*p*-TS). The conductivity was found in the range of 61.3 S/cm to 23.6 S/cm with different concentrations of (*p*-TS) being used to prepare the composite films. Generally, the existence of dopant (*p*-TS) may cause the creation of positively charged polypyrrole causing more electron holes to be available for longer polymer chains, and more co-

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planarity between inter chains, which are all favorable for a higher conductivity performance (Kassim et al., 2006).

The presence of the anions as dopants in the polymer matrix has made the thermal stability of these polymers more complicated than conventional polymers. Ansari, (2006) has also found that mild thermal treatment of polypyrrole conducting polymers in inert atmosphere, the electrical conductivity can be improved. The increase in conductivity may be related to annealing effects which improves the local ordering within the film and also the removal of non-polymeric impurities trapped into the polymer matrix during growth. However, the amount of conductivity change is greatly dependent on the nature of the dopant anion incorporated during growth. However; at elevated temperatures, structural changes such as crosslinking or chemical interactions between counterion and polymer that leads to blocking charge carriers' paths or shorten conjugated system will also result to a decrease in electrical conductivity.

Introduce the insulating polymeric matrices into the conducting polymers which is due to the excellent process ability of classical insulating polymers. This process can be achieved by blending, composite formation or co polymerization. Co polymerization could be more desirable way because the chemical linkage between the insulating matrix and the conjugated polymer can improve the chemical stability of the polymer. The resulting copolymers with new functional groups then showed different properties from polypyrrole homopolymers, which would probably widen the application of conducting polymer. Several types of copolymers containing pyrrole and other insulating units, such as styrene, tetrahydrofuran, methyl methacrylate, ε-caprolactone, acryloyl chloride, etc., have been prepared and studied. All results have shown the success in improving the-

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mechanical and physical properties of polypyrrole. However, these synthetic methods contained many restrictive steps and strict conditions, which then lead to a limited application of these copolymers. A simple and alternative way is direct electrochemical co polymerization of monomers present in the mixture of a proper solution (Belmokhtar et al., 2007).

Bai and Shi, (2007) also reported, that the incorporating of a second component into a conducting polymer film is one of the most critical methods used to develop new sensors. In comparison with the modification of molecular structure of conducting polymers, the advantage of this technique is that it can side step complicated chemical syntheses. The functions of incorporating another component into the conducting polymers are manifold. That can then be used to classify these sensors according to their sensing mechanisms. In some cases, the second components play an important role in the sensing process. They may improve the properties of the sensing film (i.e. its partition coefficient) which then helps in an electron or proton transfer, or they can directly interact with analytes by the process of swelling or electron/proton exchange.

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An application of conducting polymers have been essentially extended during the last few years and now includes many divers different fields of science and technology such as corrosion protection and anti static coatings, applications in biosensors for the coupling of electron transfer, for immobilization of biomolecules or as selective filters, preparation of pH or reference electrodes, development of ion-exchangers and catalysts, fabrication of electrochemical windows and gas sensors (Entezami & Massoumi, 2006).

The effective detection of chemicals in the environment requires a simple yet rapid, sensitive and selective analytical sensor. Such devices should be able to continuously monitor our surroundings and give us early warnings about the level of toxic chemicals in our workplaces, factories, and homes, even when they are present in extremely low concentrations (Flueckiger et al., 2009).

The most important term in industrial senses technology is the crosssensitivity of the sensors. It defines the inclination of a particular sensor to exhibit a change in signal in an environment where many various species are present. The idea of the electronic nose emerged from the fact that gas sensors exhibit natural cross-sensitivity, but in the case of sensors dedicated to liquid samples the need for the development of new cross-sensitive materials appeared (Ciosek & Wroblewski, 2007).

In both the "tongue" and "nose" strategies, the strategic idea is not to measure single chemical components but to get images of more general and usually "human" related qualities (such as taste, odor, ripeness, quality, etc.) common to intricate systems. When comparing these two areas, more references are found in the field of electronic noses, but it can be noticed an increasing interest in the development of electronic tongues or taste sensors. Such recent advances have been applied, for instance, for classifying food, drinks, water, etc (Legin et al., 1997).

The e-tongue system comprises an array of capacitive sensors having different responses and properties when immersed in different chemical solutions. The measured values of electric capacitance for each unit represent the variation on the physical-

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chemical characteristics of sampled solutions. The e-tongue name refers to the human tongue, which contains countless receptor molecules that trigger nerve signals when they encounter taste-imparting molecules thus detecting different tastes such as sweet, salty, sour and bitter (Riul et al., 2003).

An application for the use of sensor arrays for the analysis of liquid samples started in the middle eighties, when Otto and Thomas, (1985) applied the principle of simultaneous measurement with several plasticized polymeric membrane potentiometric sensors for the detection of Mg^{2+} ions concentration in multicomponent solutions of a composition similar to biological liquids (blood plasma and urine). An accurate detection of magnesium ion concentration in biological liquids is of vital importantnce especially due to an absence of highly-selective Mg^{2+} electrodes which may then permit a direct measurement of Mg^{2+} on the high background concentration of calcium. After this pioneering work done, many applications of multisensor arrays for liquid phase analysis have been reported both for qualitative discrimination and quantitative determination of various components and several comprehensive reviews were published. Multisensor arrays composed of various types of electrochemical sensors and using different detection principles were devised (Legin et al., 2003-Albert & Lewis, 2000). Thus, an array based on sensors with polymeric lipid membranes was reported by Toko et al., (1990) from Kyushu University, Japan. Such a system was called a "taste sensor", since it showed an ability to distinguish 5 basic tastes: sweet, bitter, salty, sour and umami. Later "taste sensor" with a global selectivity similar to a human perception principle and commercial versions of a 'taste sensor' was reported.

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In the last few years, several research efforts have been focused on the analysis of wines applying chemical sensor arrays. Thus, Parra et al. (2006) studied the application of a voltammetric hybrid electronic tongue, composed of phtalocyanines-based carbon paste electrodes (CPEs) and gold electrodes covered by polypyrrole doped with several counter ions to be used, for the detection of forbidden adulterants in wines, used to improve wine organoleptic characteristics. The same authors then developed an array of CPEs modified with three rare-earth bisphthalocyaninate compounds and successfully applied it for the discrimination of different Spanish red wines, prepared from the same grape variety but from different geographic areas and with different aging times, from 4 to 36 months.

Martinez, et al. (2005) reported that the electronic tongue developed at Linkoping University, consisted of an array of different inert metal electrodes and based itself on pulsed voltammetry and this has been used for analysis of liquid samples.

In this work, we have reported an entirely new approach to synthesize the conducting polymer composite for an electronic tongue system. The incorporating of silicon dioxide and poly (vinyl chloride) in polypyrrole doped (PPy+CB) was carried out by using polypyrrole doped conducting polymer as matrix filled by silicon dioxide with a different filler loading, the addition of the poly (vinyl chloride) was used as a binder to improve the adhesive properties of composites. This blend was produced to use as sensor layer for ionic solutions detector. The conducting composites were characterized and determined the effect of filler loading and concentrations of some ionic solutions.

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1.2 Objectives

1.2.1 To study the functional group of polypyrrole /poly (vinyl chloride) blends with different SiO_2 loading.

1.2.2 To analyze the surface morphology of polypyrrole /poly (vinyl chloride) blends with different SiO_2 loading.

1.2.3 To study the crystallography of the polypyrrole /poly (vinyl chloride) blends with different SiO_2 loading.

1.2.4 To determine the glass transition temperature and melting pointe of polypyrrole /poly (vinyl chloride) blends with different SiO_2 loading.

1.2.5 To study the effect of silicon dioxide on the electrical conductivity of PPy /PVC-SiO_2 blends at different loading as conducting polymer for ionic solution detector.

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CHAPTER 2

LITERATURE REVIEW

2.1 Conducting Polymers

Polymers have always been considered as an insulator of electricity. No one would have believed 30 years ago that polymers could conduct as well as metals. This brought to life through simple modification of ordinary organic conjugated polymers. This well known electrically nowadays by conducting polymers or synthetic metals, according to Bakhshi and Bhalla (2004), these materials combine the electrical properties of metals with some of polymers features such as, weight, workability, resistance to corrosion and chemical attack and lower cost. These features allowed these materials to penetrate the daily life with a wide range of products, extending from daily common consumer goods to highly specialized applications in space, aeronautics, electronics, and non-linear optics. It is, therefore, no wonder that these polymers are called the materials of the twenty-first century.

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Polymer (material containing a long chain of molecular structures) is by default an insulator. The initial motivation for developing and studying these materials, were due to their wide application as an insulating material, these materials are widely used for insulating electric wires, and cases for electrical appliances to prevent human from direct contact with electricity. The idea of conducting polymers or plastic can be absurd. Approximately three decades ago, scientist discovered a process that makes

structural adjustment for a set of conjugated polymers that could transfer it from insulators to highly electrically conductive materials, this process is well known by doping, and these new resulting materials carried the name of 'polyacetylene' (Silbey et al., 1982).

Conducting polymers are often called 'synthetic metals', beside their mechanical properties of conventional polymers; they have some electrical, electronic, magnetic and optical properties inherent to metals or semiconductors. These properties are intrinsic to the doped material; these properties are different from the one originating from mixing non-conductive polymers with any type of conducting materials. The conductivit in intrinsic polymers are assigned to the delocalization of π-bonded electrons over the polymeric backbone; these properties will add extra features to the polymers that are similar in its essence to the electronic one, such as low energy, low ionization potentials, optical transitions and high-electron affinities (Patil et al., 1988).

The electrical conductivity of polymers can be categorized as semi conducting materials. The best way to justify their electrical conductivity is in terms of the band gap, which is similar to semiconductors. In semiconductors with small-band gap, the gap between the valence band or lowest unoccupied molecular orbital (LUMO) and the conduction band or highest occupied molecular orbital (HOMO) is small. When doping the polymers with foreign conducting atoms (dopant), the number of charge carriers will increase, accompanied with the formation of a charge transfer complex. The result is the creation of highly delocalized radicals. Cationic radicals are formed from acceptor dopants while anionic radicals result from dopants that donate electrons. Oxidative doping results in the creation of new low energy transitions due to bipolaron production

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