Preparation and Characterization of Poly(Ethylene Oxide)(MW 35K and 100K)/ Silica Nanoparticle Composites

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ABSTRACT

DEPARTMENT OF CHEMISTRY

ALFINAIKH, REEM S. B.S. UMM AL-QURA UNIVERSITY, 2009

PREPARATION AND CHARACTERIZATION OF POLY(ETHYLENE OXIDE)(MW 35K AND 100K)/ SILICA NANOPARTICLE COMPOSITES

Committee Chair: Ishrat Khan, Ph.D.
Thesis dated December 2017

In recent years, polymer-inorganic nanoparticle compositions have been a subject of considerable interest in order to achieve desired chemical, physical properties and mechanical properties. In this study a polymer nanocomposites have been prepared by incorporating silica nanoparticles (~20 nm) as fillers into poly(ethylene oxide) matrix. The composites of poly(ethylene oxide) and silica nanoparticles were prepared by solution blending. The product composites were powders. The thermal properties of the composites were investigated using the Differential Scanning Calorimetry. The Nuclear Magnetic Resonance ($^{13}$C solid state, $T_1\rho$), Atomic Force Microscopy, X-ray diffraction and Fourier Transform Infrared Spectroscopy were used to investigate the effect of the nanoparticles on the polymer matrix. The results suggest that the silica nanoparticles were reasonably well dispersed in the PEO 35K. The dispersion was accompanied by slightly reduced the crystallinity. However, with increasing the SiO$_2$ nanoparticles the aggregation Phenomenon appears. Moreover, with increase in the MW of the PEO to 100K the dispersion of the nanoparticles decreased and aggregation phenomenon is observed even at lower of SiO$_2$ contents.
PREPARATION AND CHARACTERIZATION OF POLY(ETHYLENE OXIDE)
(MW 35K AND 100K)/SILICA NANOPARTICLE COMPOSITES

A THESIS
SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

BY
REEM SULIMAN ALFINAIKH

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA
DECEMBER 2017
ACKNOWLEDGEMENTS

First, I would like to thank my advisor, Dr. Ishrat Khan, for believing in me and for giving me the opportunity to work under his supervision. I would like to express especial thanks to my committee members Dr. James Reed and Dr. Cass D. Parker for their valuable guidance. I would like to thank Dr. Zhou for his training and help with SiO$_2$ and the AFM; Dr. Biswajit for assistance with using the NMR; Ian Stubbs for training with the FT-IR; William Simmons for the training to use the DSC instrument; and John Melnyczuk for the assistance and help with the XRD.

A special thanks to my lovely father, Suliman Alfiinaikh, my mother, Haya Almuhaisen, my sisters, Ruba and Rasha, and my brothers, Mohammed and Meshal, for their support and encouragement. I would like to thank my amazing husband, Ayman, for his patience and support. I want to acknowledge the source of my inspiration my sons, Abdulrahman and Omar.

I would like to express especial thanks to my sponsor the King Abdullah Scholarship that gave me the opportunity to continue my studies abroad.

I would like to express my thanks to Wafa Almutairi and everyone whose entry into my life has supported and motivated me to meet my objectives.
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<thead>
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<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAU</td>
<td>Clark Atlanta University</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>35K</td>
<td>PEO of number average molecular weight 35,000 g/mol</td>
</tr>
<tr>
<td>100K</td>
<td>PEO of number average molecular weight 100,000 g/mol</td>
</tr>
<tr>
<td>PNCs</td>
<td>Polymer Nanocomposites</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Silica Nanoparticle</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>PNCs</td>
<td>Polymer Nanocomposites</td>
</tr>
<tr>
<td>SPEs</td>
<td>Solid polymer electrolytes</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>SsNMR</td>
<td>Solid-state Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>$T_{1p}$</td>
<td>Spin-lock rotating frame relaxation rate</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning Calorimetry</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>e.g.</td>
<td>exempli gratia</td>
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CHAPTER I
INTRODUCTION AND BACKGROUND

A polymer is a large molecule composed of simple repeating units called monomers. The molecular weight of a polymer is usually in the range of several thousand to several million atomic mass units. There are many important polymers that exist in nature such as cellulose and proteins. However, the chemical industry has developed many technologically important polymers such as plastics and elastomers, which allow us to live; in what may be called the polymer age.\(^1\) The term polymer was introduced by Berzelius in 1883.\(^2\) Polymers may be thermoplastics, thermosets or elastomers, depending on their mechanical and thermal properties.\(^2\)

Polymers have numerous applications. This is especially true for solid polymer electrolytes (SPE). For example, the demand and need for zero-emission vehicles has motivated researchers to develop batteries with high energy densities, long life, reliability, and safety.\(^3\) Solid polymer electrolytes with appropriate properties e.g. conductive and mechanical properties, are being developed and in most instances the SPE uses poly(ethylene oxide) as the matrix material.

1.1 Poly(Ethylene Oxide)

Poly(ethylene oxide) (PEO) was discovered by Laurenco in 1860 by the condensation of ethylene glycol and ethylene dibromide. However, the first high
molecular weight poly(ethylene oxide) was prepared by Staudinger. It was also the first polymer to be cross-linked by radiation. Currently, poly(ethylene oxide) is available in a wide range of molecular weights, ranging from a few hundred to several millions grams/mole.

The lower molecular weight polymers are often referred to as polyethylene glycol (PEG), and the higher molecular weight polymers are normally referred to as poly(ethylene oxide), poly(oxyethylene) or polyoxirane. Poly(ethylene oxide) is a polyether with the formula, H-(O-CH2-CH2)n-OH. A polymer can have different morphologies, which are not only a function of the type of monomer but also of the molecular weight of the polymer. For example low molecular weight polyethylene glycol is amorphous at room temperatures, but higher molecular weight poly(ethylene oxide) contains both amorphous and crystalline domains. This gives the polymers complex properties, because it is partially crystalline and partially amorphous. PEO is generally classified as a thermoplastic polymer. Ethylene oxide is the monomer that can be used to synthesize poly(ethylene oxide). It is a three-member ring with the molecular formula, C2H5O. See Figure 1.

![Ethylene oxide and Poly(ethylene oxide)](image)

**Figure 1.** Chemical structure of ethylene oxide and poly(ethylene oxide).
The ring is highly reactive and can be used to carry out ring-opening polymerizations.

The ethylene oxide monomer can be prepared in two ways.\textsuperscript{3} It may be prepared in a two-step synthesis by first forming ethylene chlorohydrins, and then the ethylene chlorohydrin is dehydrohalogenated in the second step. See Scheme 1.\textsuperscript{1,3}

\[
\text{H}_2\text{C}═\text{CH}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{ClCH}_2\text{CH}_2\text{OH} + \text{HCl}
\]

\[
2\text{ClCH}_2\text{CH}_2\text{OH} + \text{Ca(OH)} \rightarrow \text{H}_2\text{O} + \text{CaCl}_2
\]

**Scheme 1.** Two-Step of Preparing the Monomer of Ethylene Oxide by Forming Ethylene Chlorohydrins, and then the Ethylene Chlorohydrin is Dehydrohalogenated.

Alternatively, it can be prepared by the oxidation of ethylene with oxygen, using a silver catalyst, as shown in Scheme 2.

\[
2 \text{H}_2\text{C}═\text{CH}_2 + \text{O}_2 \stackrel{\text{Ag}}{\longrightarrow} 2 \text{H}_2\text{O}
\]

**Scheme 2.** Preparing the Monomer of Ethylene Oxide by the Oxidation of Ethylene with Oxygen using a Silver Catalyst.

Poly(ethylene oxide) can be synthesized from the monomer, ethylene oxide, by either anionic or cationic ring opening polymerization. The preferred method is the anionic ring opening polymerization, because the polymerization is fast and high molecular weight polymers can be synthesized. The cationic polymerization is difficult to control.\textsuperscript{3} High molecular weight PEO has been synthesized using potassium hydroxide as the initiator.\textsuperscript{1,3}
The mechanism for the anionic polymerization of ethylene oxide is depicted in Scheme 3.

Scheme 3. Mechanism for the Anionic Polymerization of Ethylene Oxide.

The anionic polymerization of ethylene oxide is efficiently carried out using KOH as an initiator. The hydroxide in a good nucleophile and the size of the potassium cation ensures the formation of a loose ion-pair, thus keeping the anion reactive during the polymerization. Bulk polymerization results in almost quantitative conversion of the monomer to the polymer.\textsuperscript{1,3,7} The mechanism for the cationic polymerization of ethylene oxide is depicted in Scheme 4.
Poly(ethylene oxide) has interesting solution properties and has the ability to complex with cationic ionic and neutral molecules. This is, because PEO has both hydrophobic and hydrophilic character. The hydrophobicity arises from the presence of the ethylene units. The hydrophilicity arises from the presence of the oxygen atom in the backbone which permits the formation of ion-dipole and H-bonding interactions with other molecules.\(^3\) High molecular PEO is a highly crystalline polymer with a melting temperature around \(68^\circ\text{C}\).\(^3\) Poly(ethylene oxide) is soluble in water at room temperature\(^3,5,7\) and in most of the organic solvents, such as dichloromethane, dichloroethane, chloroform, and the benzene.\(^3\) By contrast the other polyethers, which are shown in Table 1, are mostly insoluble in water. Therefore, the water solubility of PEO is a quite unique and important property.\(^7\)
Table 1. The Solubility of Different Polyethers in Water

<table>
<thead>
<tr>
<th>Polyether</th>
<th>Formula</th>
<th>Solubility in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (ethylene oxide)</td>
<td>(-CH₂CH₂O-)ₙ</td>
<td>Soluble</td>
</tr>
<tr>
<td>Poly (methylene oxide)</td>
<td>(-CH₂O-)ₙ</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Poly acetaldehyde oxide</td>
<td>(-CH(CH₃)O-)ₙ</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Poly (propylene oxide)</td>
<td>(-CH₂CH₂(CH₃)O-)ₙ</td>
<td>Partially soluble</td>
</tr>
<tr>
<td>Poly (trimethylene oxide)</td>
<td>(-CH₂CH₂CH₂O-)ₙ</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Poly (tetramethylene oxide)</td>
<td>(-CH₂CH₂CH₂CH₂O-)ₙ</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

PEO is used in many different applications, because of its unique properties, such as its ability to complex with small molecules. For example, PEO complexes with different alkali metal salts and is used as solid electrolytes in solid-state lithium ion batteries.\(^{11-15}\) Additionally, PEO is biocompatible and is the polymer of choice in many biomedical applications. The water solubility and low toxicity of PEO makes the polymer a good choice for biomedical applications such as drug delivery.\(^{7,16-22}\) PEO finds a variety of applications depending on its properties as crystallinity and molecular weight.\(^8\) High molecular weight PEO can be used in hydrogel products,\(^7,8\) building materials, body care products, mining, papermaking, and tablet binders.\(^7\)

1.2 Nanotechnology

The term nanotechnology was introduced in the 1990s and is defined as, “The creation, processing, characterization, and utilization of materials, devices, and systems with dimensions on the order of 0.1-100 nm, exhibiting novel and significantly enhanced
physical, chemical, and biological properties, functions, phenomena, and processes due to their nano-scale size. The use of nano-scale particles is not new in polymer science. During the past decade nanotechnology has entered every aspect of science and technology from chemistry to biology to electrical materials. Inorganic nano-scale materials include nanoparticles composed of metals (e.g., Au, Fe), metal oxides (e.g., SiO$_2$, TiO$_2$), and nanotubes. The choice of the optimal nanoparticle depends on the target thermal, mechanical and electrical properties. The size of a nanoparticle, by definition, must be less than 100 nm in at least one dimension (Figure 2). Compared to the bulk scale, the properties of materials at the nano-scale can be distinctly different. The properties at the nano-scale are size, shape and crystal structure dependent. The smaller the size of the nanoparticles, the larger is the surface area per unit volume. Because of the large surface area to volume ratio, nanoparticles at extremely low content in a polymer matrix can have remarkable effect on the physical and material properties of polymers.

Figure 2. Nanoparticles, nanoplatelets, nanotubes 4 nm, silicon dioxides 200 nm.
Nanoparticles have properties that cannot be achieved at the macro-scale (bulk materials). Various nanoparticles can impart different properties to the nanocomposites. They impact such properties as electrical and thermal conductivity, thermal stability, density, mechanical properties (e.g. stiffness, and fatigue) and physical properties (e.g. magnetic, and optic). Nanotechnology has a broad range of applications, such as in medicine (drug delivery), cosmetics, agriculture, optics, food packaging, wastewater treatment and electronic devices.

1.2.1 Silica Nanoparticles

Silicon Dioxide is also known as silica. The simplest way to prepare silica is by exposing silane to oxygen at ambient temperature (Scheme 5).

\[
\text{SiH}_4 + 2\text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}
\]

**Scheme 5.** The Simplest way to Prepare Silica.

Silica has been used in polymers as a reinforcement material. The effect of nanoparticles as fillers depends on the resin system, particle size, surface area, loading and surface modification. Due to the high bond energy of the Si-O bond, SiO\(_2\) has extremely high thermal stability. When silica is dissolved in water, it can be found in three forms: colloidal, suspended particles, and reactive particles.

The properties of silica nanoparticles (nSD) depend on the condition used in the synthesis such as the temperature, time of precipitation, pH and modes of washing and drying. These factors influence properties of the SiO\(_2\) nanoparticles such as size, degree of aggregation, specific surface area, and inner-surface hydrophobicity. Silicon dioxide has a number of advantageous properties, such as high-purity, optically
transparency, non-toxicity, and homogeneity.\textsuperscript{22} Silicon dioxide has various applications as fillers in rubber and plastics, drying powders, substrates for catalysts, anticorrosion agents, drug-delivery etc.\textsuperscript{4,22}

1.3 Polymer Nanocomposites

In order to develop polymers with desirable properties for particular applications, engineers and scientists have developed nanocomposites.\textsuperscript{5} When an organic polymeric material and inorganic nanoparticles (less than 100 nm at least in one dimension) are combined, the resulting material is called a nanocomposite.\textsuperscript{25,28,34} By combining the core characteristics of the polymer, such as flexibility, ductility and processability and the core characteristics of the inorganic materials, such as rigidity and thermal stability, these separate characteristics can be synergistically integrated within nanocomposites having desired properties.\textsuperscript{35}

Polymer nanocomposites have a long history. However, a sudden increase in interest occurred, when researchers at Toyota reported in 1990 that beneficial results could be achieved, by reducing the size of the inorganic particle.\textsuperscript{10,16} Polymer nanocomposites can be found in everyday life, because of the advantages that a polymer nanocomposite has, such as flexibility, high strength, low weight, faster assembly, etc.\textsuperscript{10} Polymer nanocomposites have applications in a variety of systems ranging from vehicles to cellular phones.\textsuperscript{36} Typical polymer nanocomposites are prepared having about 5\% nanoparticle fillers in the polymer matrix.

Nanocomposites consist of two or more chemically and physically different components, the matrix and the filler. The matrix and the filler are separated by a distinct
interface. The matrix is continuous and present in greater quantity. Therefore, the essential purpose of matrices is to distribute the fillers uniformly. The fillers are discontinuous and are usually stronger than the matrix material. Thus, it is called reinforcing phase. The goal of the fillers is to improve strength by enhancing the matrix elastic modulus,\textsuperscript{24,25} stiffness, toughness and dimensional stability\textsuperscript{25} without diminishing the other properties such as the density, toughness and processibility.\textsuperscript{27} There are various matrices, such as polyesters, polysaccharides and polynucleic acids and there are various types of fillers, such as nanotubes, clay nanoparticles, metal nanoparticles, nanofibers, and hydroxyapatite. Nanocomposites can be formulated that have structures that are dimensionless (e.g. embedded cluster), one-dimensional (1D) (e.g. nanotubes), two-dimensional (2D) (e.g. nano-scale coatings) and three-dimension (3D) (e.g. embedded network).\textsuperscript{37} The sizes of nanocomposite particles do not have to be nano-scale, but can be in the macroscopic scale.\textsuperscript{26}

1.3.1 Challenges in Polymer Nanocomposites

One of the main problems in preparing nanocomposites is aggregation of the nanoparticles, the difficulty in dispersing the nanoparticles as fillers in the polymer matrix.\textsuperscript{4,16,26,31,38} The higher the surface energy differences that the filler has compared with the matrix,\textsuperscript{29} the more difficult is the dispersion. Aggregation occurs, when smaller nano-scale particles combine to form larger and larger particles.\textsuperscript{4} The second consequence is that the filling degree is low because of many factors such as the friction between the particles\textsuperscript{31} the hydrogen bonding between the particles\textsuperscript{31} and van-der-Waals forces between the particles.\textsuperscript{31,38} Van der Waals forces often cause nanoparticles to have
greater affinity for each other than for the matrix, which leads to the agglomeration phenomena. The degree of the agglomeration depends on the method that is used in preparing the nanocomposite and the specific surface area of the filler. There is a direct correlation between the specific surface area and the degree of filled composites. The larger the specific surface area of the nanoparticles, the greater is the interface between the polymer (shell) and the filler (core). However, the larger the surface area of the nanoparticles, the greater is the tendency to cluster. Another drawback is the difficulty in predicting the nanocomposites’ properties. One way to solve the aggregation problem is by surface modification of inorganic nanoparticles.

1.3.2 Composite Types

The type of composite plays a major role in determining the properties and the application of the material. The major types of composites are described below.

Polymer-matrix composites - a classical way of preparing nanocomposites, in which the agglomerated isolated nanoparticles are dispersed in a polymer matrix.

Composite nanoparticles - It is a special type of nanocomposite, in which the polymer and the nanoparticle interact as core and shell. It is called hybrid nanoparticles, when the core is an inorganic nanoparticles (e.g. silica nanoparticle) and there is an organic shell (e.g. polyethylene oxide). A major application of this type of nanocomposite is in lithium-ion-batteries.
Microsphere composite nanoparticles - microsphere nanocomposite is large sphere containing nanoparticles.\textsuperscript{31}

**1.3.3 Preparation Methods of Polymer Nanocomposites**

There are three synthetic methods that have been used to prepare this type of nanocomposites. The method of choice depends on the type of polymer matrix.

**Ex-situ formation solution dispersion** - In this method, the inorganic nanoparticles are synthesized, and then they are added to the polymer solution or melt.\textsuperscript{38} See Figure 3. However, in this process, it is difficult to gain a homogenous dispersion.\textsuperscript{38}

![Figure 3. Method for preparation of nanocomposites: solution dispersion, reprinted from Ref. 38.](image)

In-situ formation sol-gel process - Chemical reactions have been used to form nanocomposites in a liquid media, or physical methods have been used to functionalize the nanoparticles as a core/shell. The nanoparticles are generated inside the polymer.\textsuperscript{31,38} In situ synthesis, which yields a hybrid polymer material, the nanoparticles are formed in
situ from a molecular precursor\textsuperscript{38} as shown in Figure 4. The nanoparticles are usually metals or metal oxides. The final product is well identified and can have a multidimensional structure.\textsuperscript{38}

![Diagram of Inorganic Nanoparticles, Melt Organic Polymer, and Hybrid Nanocomposite](image1)

**Figure 4.** Methods for preparation of nanocomposites: In-Situ process melt dispersion, reprinted from Ref. 38.

Sol-gel process – The sol-gel process has two main steps: sol and gel. A sol is a colloidal suspension of solid particles in a liquid phase and the main purpose of gel is to bind the phases together as network.\textsuperscript{38} See Figure 5.

![Diagram of Inorganic Alkoxide, Organic Polymer, Oxide Polymer Bonds, and Hybrid Nanocomposite](image2)

**Figure 5.** Methods for preparation of nanocomposites: Sol-Gel process, reprinted from Ref. 38.
Polymer blends nanocomposites. Blending is an efficient way to combine the desirable properties of the polymer and nanoparticles. This method is less time consuming compared to the other methods and it is much cheaper. Polymer blend nanocomposites can be either homogeneous or heterogeneous. In homogenous composites the nanocomposites have the properties of both the polymer and the nanoparticles. In a heterogeneous blend the polymer and the nanoparticles properties are present in the nanocomposites. The mixing is accomplished by either solution blending or melt blending.

1.3.4 Characterization of Polymer Nanocomposites

The main goal of chemical characterization is to provide an accurate description of the properties of nanocomposites. Polymers nanocomposites can be characterized using a variety of techniques, such as the scattering techniques (X-rays scattering), microscopic techniques (SEM and TEM), and spectroscopic techniques (FTIR and NMR).

1.3.5 Properties/Applications of Polymer Nanocomposites

There has been considerable interest in polymer nanocomposites because of their low cost, high strength, stiffness, fracture resistance, abrasion resistance, impact resistance, corrosion resistance, and fatigue resistance. Because of these excellent properties, there are a variety of different applications. The applications of nanocomposites are varied depending on each individual polymer matrix (e.g. thermoplastic polymers, thermosetting polymers and elastomers). Additionally, the properties are dependent on the characteristics of nanoparticles (e.g. the particle size,
shape, chemical nature, amount, and the specific surface area). A number of factors affect the nanocomposites’ properties. For example, the type and concentration of the nanoparticles, the presence of the active groups on the surface, and the specific surface area.

Nanotechnology has become instrumental in the development of more advanced energy storage devices by increasing the energy density, power and safety of batteries such as the lithium-ion-batteries. Polymer electrolyte nanocomposites have many desirable properties such as light weight and ion exchange capacity. Polymers with the ability to ion exchange protons are promising for fuel cell applications, due to their favorable mechanical properties and high the proton conductivity. Nanocomposites have been used in the manufacturing of vehicles in order to reduce weight and improve vehicle safety, fuel efficiency and performance. The use of polymer nanocomposites can reduce the consumption of gasoline by about 5.5 billion gallons annually, thus, reducing annual CO₂ emissions by 47 million tons. Polymer nanocomposites have antimicrobial/biocidal activity, and are used in implantations, bone repair and drug delivery.

1.4 PEO/SiO₂ Nanocomposites

As interest in high quality devices grows, the need for clean energy has been increasing. Solid-state devices are the cleaner, safer, have higher performance, and are efficient compared to the devices that have liquid components. The electrolyte materials that have been used in solid-state devices must have the appropriate properties such as chemical and mechanical stability and the electrical conductivity.
electrolytes (SPE) have the advantage of easy fabrication into a wide variety of shapes and sizes, long lifetime, and leak-proof construction.\textsuperscript{41}

Since Fenton et al. discovered the ionic conductivity of poly(ethylene oxide) in 1973, the development of PEO electrolytes has passed through three stages: dry solid state polymers, gel/plasticized polymers and polymer composites.\textsuperscript{7} PEO has poor ionic conductivity at room temperature due to the semicrystalline nature that PEO because of poor chain motion.\textsuperscript{7,12,41} One way to reduce the PEO matrix’s crystallinity is to use inorganic materials with a very low inorganic content and thus enhancing the conductivity.\textsuperscript{12}

Poly(ethylene) oxide is the most utilized polymer in polymer electrolytes. PEO is compatible with a variety of polar nanofillers and chemical compounds. PEO is crystalline, producing particularly large spherulites and is soluble in polar solvents and non-polar solvents.

There are two main kinds of electroactive polymers of interest: the electronically conductive polymers and ionic conductive polymers. The ionic conducting polymers are defined as polymers, “in which the basic transport mechanism is by ion movement through the matrix”.\textsuperscript{11} Conductivity in the PEO/SiO\textsubscript{2}/alkali salt systems is the result of the movement of ions among the polymer chains.\textsuperscript{12,41}

There are two main factors that determine the performance of the SPEs, the degree of amorphousness of the polymer and the ion activity or mobility.\textsuperscript{12} In the amorphous phase the conductivity is two or three orders of magnitude higher than in the crystalline phase.\textsuperscript{41}
PEO/SiO$_2$/ alkali metal salt nanocomposites can be used in various electrochemical devices such as batteries, fuel cells, and displays.$^{43}$ In addition, PEO/SiO$_2$ is a biocompatible nanocomposite and can be used in drug delivery.$^{22}$ In addition, they can be used in tissue engineering.

1.5 The Goal of This Investigation

The objective of this study is to determine how the interaction between the polymer, PEO, and silica nanoparticle (SiO$_2$) affect the properties of PEO by decreasing it crystallinity and its glass transition temperature.$^{41}$ It is necessary to increase the content (fraction) of the amorphous phase in the PEO matrix in order to increase its conductivity for its use as a solid electrolyte.$^{41,43}$ However, in the most recent work, the addition of the fillers could not convert the crystalline phase into an amorphous phase completely and most likely this was because of the agglomeration of the nanoparticles.$^{41}$ A variety of methods can be used to guarantee a homogeneous dispersion of the nanoparticles. In this thesis nanocomposite materials were prepared using blending method and a goal of understanding the interaction between the nanoparticle and the polymer matrix. Good interaction between the two components should result in good dispersion and thus the amorphous content of the polymer should be increased in the matrix.
CHAPTER II
MATERIAL AND METHODS

2.1 Materials

All reagents were purchased from commercial suppliers and were used with purification unless otherwise specified. Poly(ethylene oxide) (Molecular Weights, 35K and 100K) was purchased from the Sigma Aldrich polymer Laboratories. Colloidal SiO$_2$ (20 nm) was purchased from Sigma Aldrich. Dichloromethane was obtained from Sigma Aldrich. Benzene was purchased from the Fisher Chemical Company. Potassium bromide (99+ %) for IR spectroscopy was acquired from Acrōs Organic Chemicals.

2.2 Methods

Silica Nanoparticles. The silica nanoparticles were prepared using the freezing-dry technique. A sample (10 mL) colloidal SiO$_2$ nanoparticles (20 nm) was frozen using liquid nitrogen and the freeze dried to obtain SiO$_2$ powders.

Poly(ethylene oxide). A 5 gram sample of PEO (35K or 100K) sample was dissolved in dichloromethane (40 mL) and then stirred at 600 rpm for 1 h at room temperature until the polymer was completely dissolved. The polymer solution was then dried overnight using an air stream to remove the dichloromethane. The samples were then dissolved in benzene (50 mL) and stirred at 600 rpm for 24 h at room temperature. The polymer solution was freeze dried to obtain PEO in the powdery form.
Preparation of PEO/SiO$_2$ Nanocomposites. A solution was prepared by dissolving 1 gram of PEO (35K or 100K) in 20 mL of dichloromethane. A second solution was prepared by dissolving 0.1 to 2.0 g of silica nanoparticles in 20 mL of dichloromethane, see Table 2. The solution were then mixed and stirred in a flask at 600 rpm for 24h at room temperature to guarantee complete reaction. The solvent was then removed by evaporation under an air stream at room temperature overnight. The samples were dissolved in 50 ml of benzene then stirred at 400-600 rpm for three days to one week. To guarantee homogeneous dispersion of the SiO$_2$ in the PEO matrix, the resulting mixture was frozen using liquid nitrogen and then dried using the under vacuum for 5-7 hours until the sample become a powder. The samples were then stored under dry nitrogen, because the nanocomposites are hydroscopic as shown in Figure 6.

Table 2. The Composition of Samples Prepared from PEO (35 K and 100K) and Silica Nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>PEO/Si-100/1</th>
<th>PEO/Si-100/2</th>
<th>PEO/Si-00/4</th>
<th>PEO/Si-100/8</th>
<th>PEO/Si-100/10</th>
<th>PEO/Si-100/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>m$_{PEO}$</td>
<td>1 g</td>
<td>1 g</td>
<td>1 g</td>
<td>1 g</td>
<td>1g</td>
<td>1g</td>
</tr>
<tr>
<td>m$_{SiO2}$</td>
<td>0.01 g</td>
<td>0.02 g</td>
<td>0.04 g</td>
<td>0.08 g</td>
<td>0.1 g</td>
<td>0.2 g</td>
</tr>
</tbody>
</table>
2.3 Instrumental Characterization Methods

There are many techniques which have been used in characterization of the nanocomposites. A number of these characterization techniques are described below.

Differential scanning Calorimetry - Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments DSC Q2000 instruments using Tzero Hermetic lids and Tzero pans under a nitrogen gas atmosphere. The DSC scans were performed on 4 - 12 mg samples and the melting temperature was determined by heating the samples to 220° C at a heating rate of 10° C/min. The samples were quenched cooled to 25° C before obtaining the heating cycle. The thermal transition temperatures that were reported are those from the second heating cycle.

Nuclear Magnetic Resonance - Nuclear magnetic resonance (NMR) rotating frame $^{13}$C spin lattice relaxation rate ($T_{1p}$) of solid samples were determined at room temperature on a Bruker AVANCE 500 MHz NMR spectrometer.

Fourier Transform-Infrared Spectroscopy – Fourier transform-infrared spectra (FT-IR) samples were crushed in a mortar and pestle with 99+% potassium bromide (KBr) until a
fine powder was obtained. The powder mixture was placed into a metal Econo mount to form a pellet by applying pressure to both ends and IR spectra were recorded.

X-ray Diffraction - x-ray diffraction (XRD) powder diffraction pattern were recorded using a 16 mm back loaded sample holder.

Atomic Force Microscopy - atomic force microscopy (AFM) was used to examine the topography of the samples. The samples were imaged with an AFM (Fast Scan Bruker) in tapping mode using a silicon tip on nitride lever to avoid surface damage.
CHAPTER III
RESULTS AND DISCUSSION

3.1 PEO/SiO$_2$ Nanocomposites

A series of PEO/SiO$_2$ nanocomposites were prepared. The molecular weights of the PEO used were 35K and 100K. The composites were prepared at different weight to weight ratios were listed previously in Table 2.

3.1.1 Fourier Transform-Infrared Spectroscopy

In Figure 7 and Figure 8, the infrared spectra of PEO 35K and PEO 100K, respectively, are shown. Of particular interest are the peaks in the 2890 and 1100 cm$^{-1}$ regions, which are assigned to absorptions from the C-H and C-O-C stretching of the polymer. The broad peak in the 3600 cm$^{-1}$ region was assigned to O-H stretching, which arise from the end groups of the polymer chain (H-(O-CH$_2$-CH$_2$)$_n$-OH).

By comparison the infrared spectrum of SiO$_2$ is relatively featureless, having a broad band in the 3700 to at 3400 cm$^{-1}$ region arising from the O-H stretching of silanol groups on the surface of the SiO$_2$ nanoparticles$^{22,33}$ (see Figure 9). The broad band in the 1212 to 1123 cm$^{-1}$ region arises from the stretching of the siloxane (Si-O-Si) bond. The band at 969 cm$^{-1}$ arises and the band at 807 cm$^{-1}$ results from the symmetric stretching vibrations. The O-Si-O bending vibrations gives rise to the band at 475 cm$^{-1}$ and the Si-OH wagging mode gives rise to the 379 cm$^{-1}$ band.$^3$
Figure 7. FT-IR spectrum of PEO 35K.

Figure 8. FT-IR spectrum of PEO 100K.
Figure 9. FT-IR spectrum of SiO₂.

Even though the chemical formula of the silica nanoparticles is SiO₂, the surfaces of the nanoparticles are covered with silanol groups, which are able to participate in hydrogen bonding. As a result the nanoparticles interact via hydrogen bonding of the silanol groups and this drives significant agglomeration. Additionally, the silanol groups should also be able to interact with the hydroxyl group and the backbone oxygen of the PEO. This should facilitate good interaction between the nanoparticles and the PEO in the composites. The interaction of the silica nanoparticles and PEO are depicted in Figure 10.
Figure 10. Depiction of the inter-particle hydrogen bonding of Si – OH (aggregation) and, weak interaction between SiO₂ and the ether oxygen of PEO by forming hydrogen bonding.

The FT-IR spectra of several PEO 35K/SiO₂ composites having different ratios (w/w) of polymer to silica nanoparticle are shown in Figure 11. The O-H stretching peak of the pure PEO 35K is weak, because there is only one O-H bond at each end of the polymer chain, H-(O-CH₂-CH₂)ₙ-OH. The wavenumber of O-H peaks for various nanocomposite may be found in Table 3. In comparison, we note the differences in the spectral features of the PEO 100K/SiO2 composites shown in Figure 12 and reported in Table 4.
Figure 11. FT-IR spectrum of labeled pure PEO 35K, and different w/w ratios of PEO35K/SiO₂ inset: magnified 1100 cm⁻¹ region.
Table 3. Infrared Spectral Data for Polymer Composites Containing Varying PEO 35K/SiO₂ Ratios (w/w)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PEO35K/SiO₂-100/0</th>
<th>PEO35K/SiO₂-100/1</th>
<th>PEO35K/SiO₂-100/2</th>
<th>PEO35K/SiO₂-100/4</th>
</tr>
</thead>
<tbody>
<tr>
<td>υOH</td>
<td>3535.2 cm⁻¹</td>
<td>3532 cm⁻¹</td>
<td>3528.9 cm⁻¹</td>
<td>3525.7 cm⁻¹</td>
</tr>
<tr>
<td>υCO</td>
<td>1099.8 cm⁻¹</td>
<td>1099.97 cm⁻¹</td>
<td>1099.67 cm⁻¹</td>
<td>1099.47 cm⁻¹</td>
</tr>
<tr>
<td>SAMPLE</td>
<td>PEO35K/SiO₂-100/8</td>
<td>PEO35K/SiO₂-100/10</td>
<td>PEO35K/SiO₂-100/20</td>
<td></td>
</tr>
<tr>
<td>υOH</td>
<td>3519.4 cm⁻¹</td>
<td>3513 cm⁻¹</td>
<td>3509 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>υCO</td>
<td>1099.73 cm⁻¹</td>
<td>1100.02 cm⁻¹</td>
<td>1099.58 cm⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

Figure 12. FT-IR spectra of pure PEO 100K, and nanocomposites at different w/w ratios of PEO 100K/SiO₂ inset: magnified 1100 cm⁻¹ region.
The FT-IR data for the composites, Figures 11 and 12 and Tables 3 and 4, shows that the intensity of OH group (~3600 cm$^{-1}$) decreases gradually with increasing amounts SiO$_2$ amount. The lowering of the frequency may suggest that a decrease in intramolecular hydrogen bonding among the silica particles and perhaps the silica silanol is interacting with the oxygen in the PEO backbone.

Table 4. Infrared Spectral Data for Polymer Composites Containing Varying PEO 100K/SiO$_2$ Ratios (w/w)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PEO100K/SiO$_2$-100/0</th>
<th>PEO100K/SiO$_2$-100/1</th>
<th>PEO100K/SiO$_2$-100/2</th>
<th>PEO100K/SiO$_2$-100/4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{\text{OH}}$</td>
<td>3524.8 cm$^{-1}$</td>
<td>3522.2 cm$^{-1}$</td>
<td>3517 cm$^{-1}$</td>
<td>3514.4 cm$^{-1}$</td>
</tr>
<tr>
<td>$\nu_{\text{CO}}$</td>
<td>1103.5 cm$^{-1}$</td>
<td>1103.4 cm$^{-1}$</td>
<td>1103.3 cm$^{-1}$</td>
<td>1101.9 cm$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PEO100K/SiO$_2$-100/8</th>
<th>PEO100K/SiO$_2$-100/10</th>
<th>PEO100K/SiO$_2$-100/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{\text{OH}}$</td>
<td>3511.8 cm$^{-1}$</td>
<td>3512.10 cm$^{-1}$</td>
<td>3501.5 cm$^{-1}$</td>
</tr>
<tr>
<td>$\nu_{\text{CO}}$</td>
<td>1101.2 cm$^{-1}$</td>
<td>1099.6 cm$^{-1}$</td>
<td>1099.1 cm$^{-1}$</td>
</tr>
</tbody>
</table>

The peaks at ~3000 cm$^{-1}$, ~1400 cm$^{-1}$, and ~1350 cm$^{-1}$ arise, respectively, from C–H bond. The position of these peaks is the same in all samples. Pure PEO has a series of peaks at 1149, 1109, 1061 and 1280 cm$^{-1}$ arising from C–H twisting. However, with the addition of SiO$_2$ nanoparticles these peaks tend to weaken and broaden, which suggest a decrease immobility of the chains in the nanocomposites compared to PEO. The peak at ~2900 cm$^{-1}$ arises from the C-H stretching of the ethylene in the PEO backbone and this peak broadens with the increase in the SiO$_2$ nanoparticle content. The reduction in the intensity of the bands in the composites compared to the pure PEO indicate that perhaps some trains to the PEO chains in the composites.
The band at 1099.80 cm\(^{-1}\) arises from the C-O-C bonds. Changes in this band are due to the formation of a hydrogen bond to the HO- groups on the surface of the nanoparticle. Thus, the spectra in Figure 11 suggest that there are possible interactions between the surfaces OH groups of the SiO\(_2\) nanoparticles and the oxygen ether in the PEO35K\(^{41}\), depicted in Figure 13.

**Figure 13.** Depiction of the hydrogen bonding between Si-OH of the nanoparticle and the ether oxygen of the PEO.
3.1.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to study the thermal behavior of the nanocomposites of various compositions and polymer molecular weights. The samples were scanned from 25°C to 220°C under a nitrogen atmosphere. The thermograms of the silica nanoparticles exhibited neither an endotherm nor an exotherm over this range (see Figure 14). Pure PEO and the nanocomposites exhibit a single endotherm (see Figures 14 and 15), which correspond to the melting temperature of the PEO in the composites. The corresponding exotherm were at a slightly lower temperature compared to the pure PEO for the composites prepared with the PEO 35K. The observation suggests both a decrease in the crystallinity of the PEO and further the crystals formed were of smaller sizes than the pure PEO.

![DSC thermograms](image)

**Figure 14.** DSC thermograms of SiO$_2$, PEO 35K, and PEO 35K/SiO$_2$ nanocomposites (100/1, 100/2) (w/w), 2$^{\text{nd}}$ heating cycle (25-220$^\circ$C/min, N$_2$ atmosphere).
Figure 15. DSC thermograms of PEO 35K/SiO$_2$ nanocomposites (100/4, 100/8, 100/10, 100/20) (w/w), 2$^{nd}$ heating cycle (25-220$^\circ$ C/min, N$_2$ atmosphere).

The DSC thermograms of pure PEO 100K and PEO 100K/SiO$_2$ composites with different compositions are shown in Figures 16 and 17. The endothermic peak is observed at 63.2$^\circ$ C which corresponding to melting temperature of pure PEO 100K. The composites show a slight shift in the melting temperature ($T_m$) towards lower temperatures on the addition of SiO$_2$. The melting temperature of the PEO 100K changes from 63.2$^\circ$ C to 58.3$^\circ$ C for the 100/20 (w/w) composite. Therefore, crystallinity of the host PEO and the crystal sizes for the PEO 100K is reduced on addition of SiO$_2$. 
Figure 16. DSC thermograms of PEO 100K/SiO$_2$ nanocomposites (100/1, 100/2, 100/4) (w/w), 2$^{nd}$ heating cycle (25-220$^\circ$ C/min, N$_2$ atmosphere).
Figures 16 and 17 show the decrease in the crystalline melting temperature with an increase of the silica content in the composite. This is similar to the observation to the PEO 35K/silica nanoparticles composites. The lowering also suggests that the nanoparticle in the polymer matrix, inhibits crystallization by decreasing the alignment of PEO chains and thus, most likely, smaller crystals are formed. The thermal data are listed in Table 5.
Table 5. Melting Points of Polymer Composites Containing Varying Amounts of SiO$_2$ Nanoparticles

<table>
<thead>
<tr>
<th>PEO35K/SiO$_2$-100/0</th>
<th>PEO35K/SiO$_2$-100/1</th>
<th>PEO35K/SiO$_2$-100/2</th>
<th>PEO35K/SiO$_2$-100/4</th>
<th>PEO35K/SiO$_2$-100/8</th>
<th>PEO35K/SiO$_2$-100/10</th>
<th>PEO35K/SiO$_2$-100/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$ ($^\circ$C)</td>
<td>66.1</td>
<td>63.4</td>
<td>61.8</td>
<td>63.8</td>
<td>62.4</td>
<td>61.6</td>
</tr>
<tr>
<td>$\Delta H_m$ (J/g)</td>
<td>1991</td>
<td>480.9</td>
<td>1970</td>
<td>1826</td>
<td>1848</td>
<td>192.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PEO100K/SiO$_2$-100/0</th>
<th>PEO100K/SiO$_2$-100/1</th>
<th>PEO100K/SiO$_2$-100/2</th>
<th>PEO100K/SiO$_2$-100/4</th>
<th>PEO100K/SiO$_2$-100/8</th>
<th>PEO100K/SiO$_2$-100/10</th>
<th>PEO100K/SiO$_2$-100/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$ ($^\circ$C)</td>
<td>63.2</td>
<td>62.1</td>
<td>59.3</td>
<td>59.2</td>
<td>58.2</td>
<td>57.0</td>
</tr>
<tr>
<td>$\Delta H_m$ (J/g)</td>
<td>3686</td>
<td>3857</td>
<td>829</td>
<td>3918</td>
<td>4450</td>
<td>3220</td>
</tr>
</tbody>
</table>

Pure PEO 35K is highly crystalline and exhibits a melting endotherm at 66.1$^\circ$C. As the silica nanoparticle content in the polymer matrix was increased, the melting temperature of the crystals decreased gradually for majority of the different compositions, see (Table 5). The data suggests that the decrease in the melting temperatures was dependent on the amount of the silica nanoparticles that are added to the PEO matrix, and that, because SiO$_2$ nanoparticles interfere with the crystallinity of the PEO, an increasingly amorphous matrix is formed.$^{36}$ This observation is consistent with earlier reports on PEO/SiO$_2$ nanocomposites.$^{36}$

The data in Table 5 is plotted in Figures 18, and 19. There is a general decrease in the melting temperature as the amount of SiO$_2$ nanoparticles increases. However, there is an increase in the melting temperature, when mPEO/mSiO$_2$ increases from 100/2 to 100/4. This anomalous behavior was reproducible, which suggests that the increase in the observed melting temperature between 100/2 and 100/4 is not an artifact. This anomalous
behavior is currently not understood. The overall shape of the DSC thermograms of the nanocomposites was similar to the neat PEO 35K.

Figure 18. DSC data of PEO 35K/SiO$_2$ nanocomposites at different w/w ratios.

Figure 19. DSC data of PEO 100K/SiO$_2$ nanocomposites at different w/w ratios.
3.1.3 \textsuperscript{13}Carbon T\textsubscript{1\rho} Relaxation Rates (Solid State)

The T\textsubscript{1\rho} spin lattice relaxation rates in the rotating frame are sensitive to motions that occur in the kHz region, and capable of distinguishing between morphologically-distinct phases, and may provide information about motional cooperativity between phases.\textsuperscript{46,47} T\textsubscript{1\rho} relaxation rates of pure PEO 35K and selected nanocomposites are listed in Table 6. The T\textsubscript{1\rho} for pure PEO 35K was 4.99 ms, but T\textsubscript{1\rho} for the nanocomposites were lower.

\begin{table}[h]
\centering
\begin{tabular}{lcc}
\textbf{SAMPLE} & \textbf{T1\rho (ms)} \\
\hline
PEO 35K/SiO\textsubscript{2} \textendash 100/0 & 4.26 \\
PEO 35K/SiO\textsubscript{2} \textendash 100/1 & 1.94 \\
PEO 35K/SiO\textsubscript{2} \textendash 100/2 & 2.47 \\
\hline
\end{tabular}
\caption{T\textsubscript{1\rho} for PEO 35K and PEO 35K Nanocomposites}
\end{table}

The decrease in the relaxation rates correlates with a decrease in the crystallinity of the nanocomposites as the silica content is increased. The general decrease in T\textsubscript{1\rho}, suggests that matrix of the composites may have increased more amorphous content. The observation that the relaxation is rate is significantly lower than that of the neat polymer also suggest that the crystals in the composites were smaller than 50 nm\textsuperscript{46,47} and the observed T\textsubscript{1\rho} is an average of the amorphous phase and the crystalline phase. The data suggests that the nanoparticles in these composites are reasonably well distributed in the PEO 35K matrix and that the SiO\textsubscript{2} nanoparticles disrupt the crystallites of the PEO 35K, which causes the decrease in the relaxation rates of the two nanocomposites. That the
relaxation rate for the composite, for which the ratio is 100/2, is higher than the
relaxation rate for composite, for which the ratio is 100/1, may possibly be the result of
increased aggregation resulting in lower dispersion. This observation may help explain
the increase in the melting temperature observed in the DSC studies, where the melting
temperature increased between the composite, in which the composition was 100/2 and
that in which was 100/4. Further studies are necessary to understand this observation.

3.1.4 X-ray Diffraction

In Figures 23 and 24 the powder x-ray diffraction pattern for the PEO and
composites samples are shown. To better understand the x-ray diffraction pattern of the
PEO nanocomposite the spectra of pure PEO 35K, shown in Figure 20, pure PEO 100K,
Figure 21, and amorphous SiO2, Figure 22, were taken. The appearance of broad peaks
in addition to some sharp ones of the pure PEO 35K and pure PEO 100K confirm that the
crystal polymer is partially crystalline and partially amorphous, Figures 20 and 21 respectively.
Strong peaks were observed for both PEO 35K and PEO 100K at 2θ value of 23° for both
copolymers. This strongly suggests that crystalline regions in the two polymers essentially
were identical.
Figure 20. XRD powder diffraction pattern of precipitated PEO 35K.

Figure 21. XRD powder diffraction pattern of precipitated PEO 100K.
The amorphous SiO$_2$ yields a broad peak with the Bragg angle centered at $2\theta = 21.8^\circ$ at room temperature as shown in Figure 22. Similar results are reported by Musić ($2\theta = 21.8^\circ$), where the SiO$_2$ was prepared by the neutralization reaction of sodium silicate with a H$_2$SO$_4$ solution.$^{33}$ Similar results are reported by Martínez ($2\theta = 23^\circ$ at room temperature), where the SiO$_2$ was prepared by the sol-gel procedure.$^{44}$

![Figure 22. XRD powder diffraction pattern of SiO$_2$.](image)

The X-ray powder diffraction patterns of the composites as shown in Figures 23 and 24 contain the same peaks as found in PEO and SiO$_2$, suggesting that there are no remarkable changes in the crystalline phases of PEO 35K and PEO 100K.
Figure 23. XRD patterns of PEO 35K, SiO₂ nanoparticles, and PEO 35K/SiO₂ nanocomposites.
Figure 24. XRD diffraction patterns of pure PEO 100K, SiO$_2$ nanoparticles, and PEO 100K/SiO$_2$ nanocomposites (different w/w ratios).

As the content of silica nanoparticles in the composites increase, some of the peaks shift to slightly lower diffraction angle as noted in Table 7. Whereas for both PEO 35K and PEO 100K there is a substantial decrease in the peak width when composites are formed, the difference in peak width among the composites is relatively small. Among the causes of broad diffraction peaks is the presence of small crystals or crystalline domains. Alternatively, broad diffraction peaks can result when the system is poorly crystallized. Thus changes in the width of diffraction peaks may reflect a change in the number of small crystalline domains in the composite.
The characteristics of the diffraction peak near $23^\circ 2\theta$ for PEO and the nanocomposites are listed in Table 7. This diffraction peak arises from a separation of 0.384 nm and therefore arises from non-bonding-intermolecular interactions. With the exception of sample PEO 35K100/4 the incorporation of SiO$_2$ does not impact this intermolecular distance, which suggests that the SiO$_2$ nanoparticles do not significantly impact the structure of the crystalline regions of the polymer. On the other hand, there is a significant change in the diffraction peak upon the addition of SiO$_2$ nanoparticles to the polymer matrix. There are two interpretations of this result. It is possible that SiO$_2$ nanoparticles are able to increase the size of or the crystallinity of the crystalline regions of the polymer. Alternatively, the SiO$_2$ nanoparticles destroy the crystallinity of the smaller crystalline regions by the interaction of these with the surface of the nanoparticle.
Table 7. The Positions and the FWHM of the Height Peak (of the PEO 35K, and PEO 100K) (Different w/w Ratios of the Nanocomposites)

<table>
<thead>
<tr>
<th>Sample</th>
<th>2Θ (degrees)</th>
<th>d (nm)</th>
<th>FWHM (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PEO 35K</td>
<td>23.155</td>
<td>0.384</td>
<td>0.794</td>
</tr>
<tr>
<td>PEO 35K/SiO₂ (100/1) w/w</td>
<td>23.1791</td>
<td>0.384</td>
<td>0.1535</td>
</tr>
<tr>
<td>PEO 35K/SiO₂ (100/2) w/w</td>
<td>23.1571</td>
<td>0.384</td>
<td>0.2047</td>
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<td>PEO 35K/SiO₂ (100/4) w/w</td>
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<td>0.1791</td>
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<td>PEO 35K/SiO₂ (100/8) w/w</td>
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<tr>
<td>PEO 35K/SiO₂ (100/10) w/w</td>
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<td>0.1023</td>
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<td>PEO 35K/SiO₂ (100/20) w/w</td>
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<td>0.1279</td>
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<td>Neat PEO 100K</td>
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<td>0.7675</td>
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<td>PEO 100K/SiO₂ (100/2) w/w</td>
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<td>0.380</td>
<td>0.2558</td>
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<tr>
<td>PEO 100K/SiO₂ (100/4) w/w</td>
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<tr>
<td>PEO 100K/SiO₂ (100/10) w/w</td>
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<tr>
<td>PEO 100K/SiO₂ (100/20) w/w</td>
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3.1.5 Atomic Force Microscopy

Figures 25 and 26 show atomic force microscope (AFM) images of PEO 35K and PEO 100K and selected composites. The image of pure PEO 35K shows a highly crystalline structure, which decreases upon the addition of the SiO$_2$ nanoparticle. The DSC results support this interpretation.

**Figure 25.** AFM images of: a) PEO 35K, b) 100/1, c) 100/4, and d) 100/20 (w/w) nanocomposites.
Figure 26. AFM images of: a) PEO 100K, b) 100/1, c) 100/4, and d) 100/20 (w/w) nanocomposites.
PEO/SiO$_2$ nanocomposites, having different w/w ratios, were prepared by blending followed by freeze-drying to ensure the best possible dispersion of the silica filler into the PEO matrix. The nanocomposites were studied by a number of different methods, thermal (DSC), $^{13}$C NMR solid-state to determine the $T_{1\rho}$ relaxation rates, atomic force microscopy, FT-IR, and XRD. The results show that the PEO 35K is better able to interact with the silica nanoparticles and to disperse the filler within the matrix compared with the PEO 100K. Additionally, work in the group by a colleague has shown that PEO samples, having molecular weights lower than 35K, are even better at interacting with the silica nanoparticles and dispersing the filler within the matrix. Therefore, these studies have demonstrated that the degree of aggregation by the silica nanoparticles is less in PEO matrices of lower molecular weight than those of higher molecular weights due to higher intermolecular interaction between the SiO$_2$ particles.
APPENDIX

DSC data of PEO 35K and nanocomposites of different w/w ratios separately:
DSC data of PEO 100 and nanocomposites of different w/w ratios separately:
REFERENCES


14. Li, J.; Khan, I. M. “Highly Conductive Solid Polymer Electrolytes Prepared by Blending High Molecular Weight Poly(ethylene oxide), Poly(2 or 4-vinylpyridine) and Lithium Perchlorate”. Macromolecules. 1993, 26, 4544-4550.


