MECHANICAL PERFORMANCE OF PVA/PAN COMPLEXED WITH ALUMINUM OXIDE (Al_2O_3) NANOPARTICLES FOR SOLID POLYMER ELECTROLYTE

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By

DAUDU SULEIMAN DANJUMAN

(40883)

Supervised by

Dr Abdulhakeem Bello

African University of Science and technology,

www.aust.edu.ng

P.M.B. 681, Garki, Abuja F.C.T. Nigeria

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BY

Daudu, Suleiman Danjuman

A THESIS APPROVED BY THE DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

RECOMMENDED: .....

Supervisor: Dr Abdulhakeem Bello

……...

Head, Department of Materials Science and Engineering

APPROVED: …….

Chief Academic Officer

……..

Date

CERTIFICATION

This is to certify that the thesis titled **"Mechanical Performance of PVA/PAN Complexed with Aluminum Oxide (Al_2O_3) Nanoparticles for Solid Polymer Electrolyte"** Submitted to the Department of Materials Science and Engineering, African university of Science and Technology (AUST), Abuja, Nigeria for the award of the Master's degree is a record of original research carried out by **Daudu, Suleiman Danjuman.**

ABSTRACT

Interest in solid polymer blends has increased due to the demand for flexible, lightweight, and long-lasting energy devices. Traditional lithium-ion batteries contain liquid electrolytes that pose a serious safety risk since they are chemically unstable due to the presence of carbonates, which are highly volatile and combustible. Thus, there is a need for the creation of solid-state electrolytes with reliable mechanical properties and a focus on safety and the environment. In this project, a polymer matrix of polyvinyl alcohol/polyacrylonitrile and aluminum oxide nanoparticles is combined together. To examine the solid polymer blend, A Fourier transform infrared resonance is used to characterize the produced films. Tensile testing and nanoindentation methods were used to measure the mechanical properties of the flexible films. polyvinyl alcohol/polyacrylonitrile based matrix with 7wt.% Al_2O_3 nano particle displayed the best tensile properties having a tensile strength, young's modulus, Ductility and a toughness of 1.062 MPa, 1.01 MPa, 288.4% and 23.5 KJ/m^3 respectively. However, the polymer based matrix with 10 wt% Al_2O_3 shows the highest value of Hardness and reduced modulus of 214.71 MPa and 6.19 GPa respectively as compared to the other compositions that was investigated.

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DEDICATION

In thanks for guiding me through this program, I dedicate this thesis to Almighty Allah (SWT).

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CHAPTER ONE

INTRODUCTION

1.1 Background

The expanding human population, which increases energy consumption, as well as the detrimental effects of an over-dependence on fossil fuels, have caused the entire world to look at alternate energy sources. Due to their reliance on weather, alternative energy sources like solar, wind, tidal, etc., would need an energy storage component [1]. The creation of energy storage systems and technologies has been one of the main areas of concentration for the past few decades in an effort to close this gap. Among the energy storage devices (supercapacitors) are batteries and electrochemical capacitors [2]. Supercapacitors (SC), on the other hand, use a surface phenomenon to store energy and are characterized by high power densities; as a result, they can be used for shorter periods of time than batteries but charge and discharge relatively more quickly [3]. As a new form of energy storage, SCs use carbon as their primary electrode material because it has excellent cycle life and the ability to deliver high power quickly [4]. As a result, SC is frequently employed in micro devices that require high power density and long cycle life, such as backup power, portable electronics, and a variety of car starting systems. Prioritizing cost, environmental compatibility, and the viability of industrial manufacturing are requirements for achieving the application of these devices [5].

Supercapacitors, batteries, and other energy storage technologies with high energy and power densities were developed in response to the rapidly expanding markets for portable gadgets and electric vehicles [6]. Despite having a high energy density, batteries' effectiveness in high power-demanding applications like load leveling and regenerative braking is limited by their unreasonably low power densities and short life cycles [7]. In contrast, supercapacitors are able to store a lot more energy than conventional dielectric capacitors and deliver power more quickly than batteries. Since they can produce energy pulses in just a few seconds or tens of seconds, they are well suited for applications that need them [8]. These distinct properties are the result of nanoscale capacitors, which are made of polarized electrode material and have a layer of electrolyte-attracted ions on their surface. The relationship between ion size and ion size at the electrode-electrolyte interface is direct [9].

When compared to the usage of liquid electrolytes, solid electrolytes (SEs) present exciting and practical options that lower the related safety hazards. Since they are less flammable, more flexible, have superior thermal stability, and are more safe than other SEs, polymer-based SEs are preferred [10]. Despite the fact that solid polymer-based electrolytes improve electrochemical performance, the comparatively low ionic conductivities and poor mechanical qualities of SEs continue to be a significant obstacle. Particle-reinforced composites have been investigated as electrolytes in polymer-based blends as a means of addressing these issues and improving the performance of SEs [11].

1.2 Problem statement

Compared to alternative electrochemical energy storage (EES) systems, it has been demonstrated that batteries and supercapacitors are the most efficient electrochemical energy conversion and storage technology for practical applications. Poor mechanical quality of SEs remains a significant barrier. It is essential to investigate the solid-state electrolyte's (SSE) mechanical properties in order to appreciate how mixtures behave to applied loads, as little attention has been paid to investigating the mechanical properties of polymer-based solid electrolytes. As a way of addressing these difficulties and enhancing the performance of SEs, particle-reinforced composites will be evaluated as electrolytes in polymer-based composites.

Research objectives

Through the following objectives, this research aims to evaluate the mechanical properties of polyvinyl alcohol and polyacrylonitrile solid electrolytes:

• The preparation of the solid polyvinyl alcohol/polyacrylonitrile electrolyte.

• Develop the necessary composite material.

• PVA/PAN/Al2O3 characterization via Fourier transform infra-red resonance spectroscopy.

• Percentage Study the influence of weight percent of Al2O3 particles on the mechanical characteristics of PVA/PAN-based solid electrolyte utilizing the Instron machine and Nano indentation.

1.3 Scope of Study

In this study, the best concentration of Al_2O_3 nanoparticles used as reinforcement in PVA/PAN blend electrolytes for energy storage devices is explored. The objective of this work is to improve

the mechanical properties of a PVA/PAN-based solid polymer electrolyte by including nanoparticles of aluminum oxide (Al_2O_3).

1.4 Organization

The order of the five chapters of this project is as follows;

- Chapter one, the introduction;
- Chapter two, the literature survey;
- Chapter three, the materials and methods;
- Chapter four, the results and discussion and
- Chapter five, consists of a summary and concluding remarks.

CHAPTER TWO

LITERATURE SURVEY

2.1 World Energy Crisis

Recognized is the significance of energy as a resource for satisfying human requirements. The satisfaction of daily needs, which cannot be met without energy, is what provides comfort and convenience to human life. This demonstrates that energy is essential for the success and productiveness of any human endeavor [12]. The world is in a state of uncertainty regarding potential energy sources that, would meet the needs of heavy energy consumers and, on the other hand, would minimize the carbon footprint in the environment to a manageable level due to the negative effects of global warming and the rapidly depleting fossil fuel reserves [4], [13].

As a result of this concern, there has been a surge in demand for technologies that can harness renewable energy sources that are clean and environmentally benign. If supplies run out and there is no other source of sustainable energy, the mankind will experience a disaster that costs live. Numerous industrialized nations have made substantial strides in this area. Contrary to what scholars, critics, and analysts assert, it is vital to remember that an energy crisis can result in inadequate electric power generation rather than being its cause [14]. In other words, an energy crisis is characterized by a lack of electrical supply or its scarcity. This influences every aspect of national development.

However, the weather-dependent nature of renewable energy sources needs the development of highly efficient and scalable energy storage technologies, such as Lithium ion batteries, supercapacitors, and batteries with suitable energy and power densities.

2.2 Energy Storage

Energy storage is the technique of collecting energy produced at one point for use at a later time to reduce mismatches between energy demand and production [15]. An accumulator, sometimes known as a battery, is a device that stores energy. Energy comes in many forms, including kinetic, latent heat, gravitational potential, chemical, electricity, and radiation. Energy storage is the process of converting energy from difficult to store forms to easier or more practical forms to store.

2.3 Electrical Energy Storage Technology Classification

Based on the type of energy stored in the system, electrical energy storage systems can be divided into five categories. These categories are:

- Mechanical
- Electrochemical
- Electrical
- Chemical
- Thermal

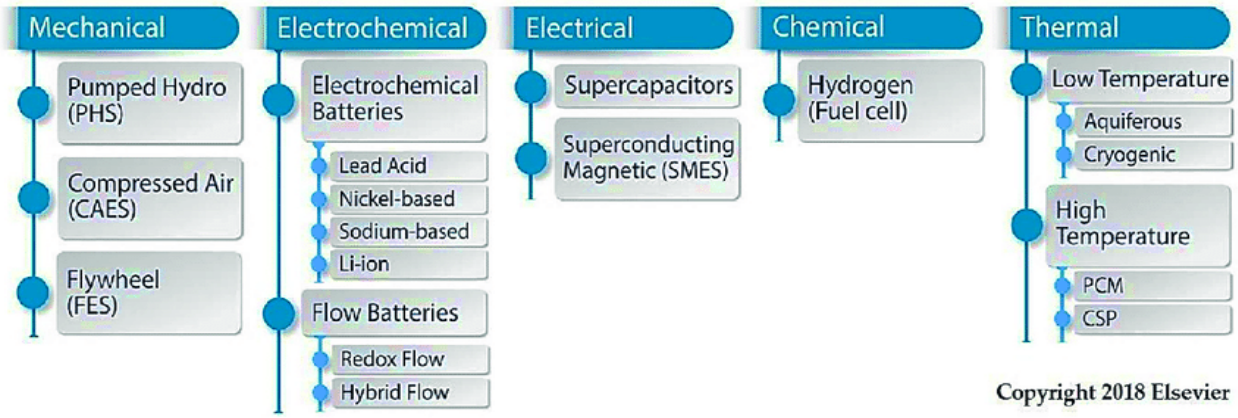


Figure 2. 1 Classification of energy storage technologies by the form of stored energy [9]

2.3.1 Mechanical Energy Storage

2.3.1.1 Pumped Hydroelectric Energy Storage (PHS)

This is a type of hydroelectric energy storage that balances the load on electrical power systems. Water is pumped from a lower elevation reservoir to a higher elevation reservoir to store energy as gravitational potential energy. During times of heavy electrical demand, the stored water is released through turbines to generate energy. Pumped-storage During peak demand, hydroelectricity allows for the storage of excess energy from continuous base-load sources such as coal or nuclear, as well as intermittent energy from renewable sources such as solar and wind. [16], [17] When compared to ordinary hydroelectric dams of comparable power output, pumped storage reservoirs are somewhat small, and production times are usually less than half a day.

The PHES has an infinite cycle stability and a high efficiency of 70% to 80%. The main disadvantages of PHES are its initial capital cost and site-specificity [18].

2.3.1.2 Compressed Air Energy Storage (CAES)

Using the potential energy of a compressed gas, this generates electrical energy. Electricity is used to compress air, which is subsequently stored in an underground system vessel or storage cavity [19]. When power is required, stored compressed gas is expanded using a typical gas turbine

expander. To generate the maximum energy, compressed air is coupled with natural gas. This technology improves green energy generation. This method provides less energy to the grid than it would without the storage device, which is a disadvantage [18].

2.3.1.3 Flywheel Energy Storage (FES)

The system functions by rapidly accelerating a rotor (flywheel) and retaining the system's energy as rotational energy. When energy is removed from a system, the flywheel's rotating speed drops; conversely, when energy is provided, the flywheel's speed increases. Typically, FES systems use electricity to accelerate and decelerate the flywheel, although certain devices also directly employ mechanical energy [20].

Modern FES systems comprise rotors that spin at speeds ranging from 20,000 to over 50,000 rpm in a vacuum enclosure and are suspended by carbon fiber composite magnetic bearings of exceptional strength [21]. Compared to conventional forms of energy storage, these flywheels can reach their maximum energy capacity in a matter of minutes [21].

2.3.2 Electrochemical Energy Storage

2.3.2.1 Battery

Batteries are a type of electrochemical storage device consisting of one or more parallel or series-connected cells that store chemical energy and convert it to electrical energy when necessary. Typically, batteries consist of at least one voltaic cell composed of an oxidation and a reduction half-cell that are separated by a semipermeable membrane (salt bath) (salt bath). In each half-cell, anode and cathode metal electrodes are present; oxidation occurs at the anode while reduction occurs at the cathode. The cathode consequently acquires electrons while the anode loses electrons. Electrolyte-containing fluid surrounds the two electrodes. When electrons flow from the anode to the cathode, the battery is powered by the resulting electricity.

The two kinds are primary batteries and secondary batteries. Electrochemical reactions that are irreversible render primary batteries disposable and nonrechargeable. Secondary batteries can be recharged since their electrochemical reactions are reversible. Wet and dry cells are two distinct battery kinds. Insulator sheets separate the anode and cathode in wet cells, which contain a liquid electrolyte. Leclanche cells, Daniel cells, and lead-acid accumulators are examples of wet cell batteries. Paste-like electrolytes are present in the dry cell.

2.3.2.2 Flow Battery

A flow battery, sometimes known as a redox flow battery (after reduction-oxidation), is a type of electrochemical cell in which two chemical components dissolved in liquids pumped through the system on opposite sides of a membrane generate chemical energy [22], [23]. Ion transfer happens across the cell membrane as both liquids circulate within their respective compartments. In real-world applications, the Nernst equation is used to chemically determine the range of cell voltage, which is between 1.0 - 2.43 V. The volume of the electrolyte affects the energy storage capacity, whereas the surface area of the electrodes affects the power.

A flow battery can be utilized similarly to a fuel cell (where used fuel is removed and new fuel is injected) or a rechargeable battery (where an electric power source drives regeneration of the fuel). Flow batteries have a number of technical advantages over conventional rechargeable batteries made from solid electroactive materials, including independent scaling of power (determined by the size of the stack) and energy (determined by the size of the tanks), long cycle and calendar lives, and potentially a lower total cost of ownership. All flow batteries, however, have a lower cycle energy efficiency (50-80%) than lithium-ion batteries.

2.3.3 Electrical Energy Storage

2.3.3.1 Capacitors

A capacitor is a passive energy storage device with two terminals. It generates a static voltage or potential difference across its plates and stores energy as an electrical charge. A capacitor consists of two parallel conducting plates separated electrically by an insulating material such as ceramic, mica, waxed paper, liquid gel, or air [24].

2.3.3.2 Super capacitors

A supercapacitor (SC), sometimes known as an ultracapacitor, is a high-capacity capacitor that connects electrolytic capacitors and rechargeable batteries. It has a capacitance value that is substantially greater than that of conventional capacitors, but lower voltage constraints. Typically, it can accept and distribute charge much more quickly than batteries, store energy 10 to 100 times more efficiently per unit volume or mass than electrolytic capacitors, and withstand significantly more charge and discharge cycles than rechargeable batteries [25].

In applications requiring frequent rapid charge/discharge cycles, such as regenerative braking, short-term energy storage, or burst-mode power delivery in automobiles, buses, trains, cranes, and

elevators, supercapacitors are utilized instead of compact long-term energy storage [17]. As backup power for static random-access memory, smaller units are utilized (SRAM).

In contrast to conventional capacitors, supercapacitors utilize electrostatic double-layer capacitance and electrochemical pseudocapacitance, both of which [26] contribute to the capacitor's total capacitance with a few differences:

• **Electrostatic double-layer capacitors (EDLCs)** separate charges in a Helmholtz double layer at the interface between the surface of a conducting electrode and an electrolyte using carbon electrodes or their derivatives. The electrostatic double-layer capacitance of these materials is significantly greater than their electrochemical pseudocapacitance. The charge separation is significantly less than that of a conventional capacitor, on the order of a few ngstroms (0.3–0.8 nm).

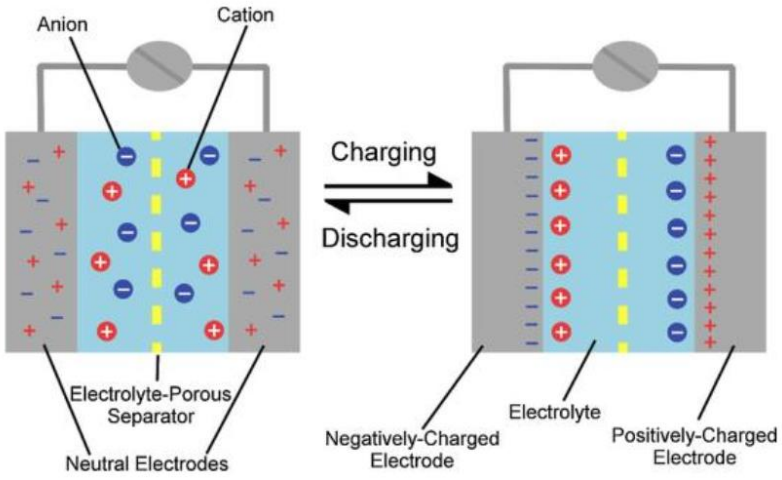


Figure 2. 2 Schematic of an EDLC [27]

- **Pseudocapacitors** employ electrodes constructed of metal oxide or conducting polymer that have a high electrochemical pseudocapacitance in addition to a high double-layer capacitance. Pseudocapacitance is produced by faradaic electron charge transfer via redox reactions, intercalation, or electrosorption. One electrode in a hybrid capacitor, such as the lithium-ion capacitor, predominantly demonstrates electrostatic capacitance, while the other primarily demonstrates electrochemical capacitance.

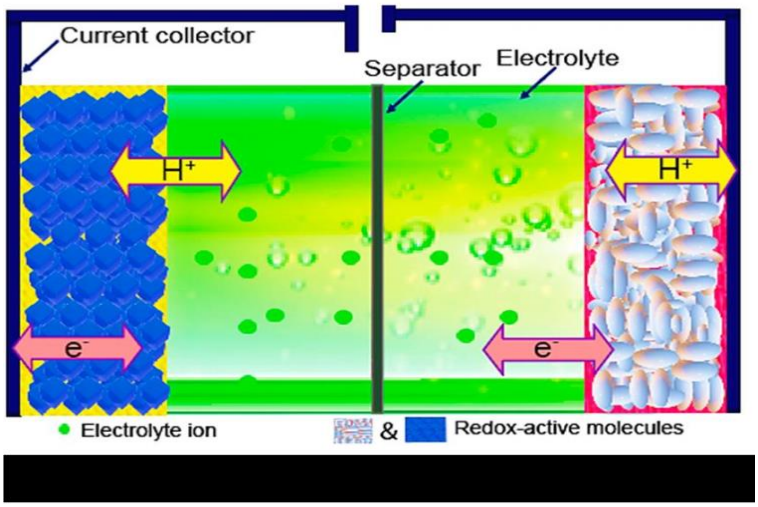


Figure 2. 3 Schematic diagram of Pseudocapacitor [27]

2.3.3.3 Superconducting magnetics

SMES devices store energy in a magnetic field generated by a direct current running through a superconducting coil cooled below its superconducting critical temperature. Typical SMES system components include a superconducting coil, a power conditioning device, and a refrigerator. After charging the superconducting coil, magnetic energy can be retained indefinitely because the current does not decay [28].

The energy can be sent to the network by discharging the coil. The accompanying inverter/rectifier is responsible for around 2% to 3% of the energy loss in each direction. Compared to other technologies, SMES loses the least amount of electricity throughout the energy storage process. The round-trip efficiency of SME systems exceeds 95% [29].

2.3.4 Chemical Energy Storage (Hydrogen)

It is applied in numerous ways to store hydrogen for future use. These include mechanical means, such as high pressures and low temperatures, and chemical compounds that release H2 when necessary. Even though enormous amounts of hydrogen are created, the most majority of it is consumed on-site, primarily for ammonia manufacturing. For use in industrial and space exploration, hydrogen has been compressed and transported as a liquid or gas in cylinders, tubes, and cryogenic tanks for decades. Interest in using hydrogen for on-board energy storage in zero-emissions vehicles is pushing the development of new storage technologies that are better suited for this new application.

2.3.5 Thermal Energy Storage

utilizing a range of approaches to attain the goal. Depending on the exact technology, extra thermal energy can be stored and utilized hours, days, or months later at scales ranging from the individual operation to the building, multiuser building, district, town, or region. Examples of uses include balancing energy demand between day and night, storing summer heat for use in winter, and utilizing winter cold for use in summer (Seasonal thermal energy storage). Storage media also include water or ice-slush tanks, masses of native earth or bedrock accessed with heat exchangers through boreholes, deep aquifers held between impermeable strata, eutectic solutions, and phase-change materials [30], [31].

Heat or cold produced by heat pumps from off-peak, less expensive electric power, a practice known as peak shaving; heat from combined heat and power (CHP) power plants; heat produced by renewable electrical energy that exceeds grid demand; and waste heat from industrial processes are other sources of thermal energy for storage. Heat storage, both seasonal and short-term, is regarded as a critical tool for integrating the electricity and heating sectors into energy systems powered almost entirely or entirely by renewable energy sources, as well as for cost-effectively balancing high shares of variable renewable electricity production [32], [33].

2.4 Gains from Energy Storage

- **Minimize Environmental Effects**

  In its most basic form, energy storage enables the saving of electricity at a later time when and place. As a result, the electric grid becomes more efficient and capable, and it can also lower greenhouse gas (GHG) emissions.

  Energy storage can aid in the integration of more solar, wind, and distributed energy resources into the grid by enhancing its flexibility. Also, it can decrease the demand for new peak power plants that release pollution by raising the capacity factor of currently available resources. This will increase the grid's efficiency. Energy storage enables more dependable and easy evolution of our energy supply mix as it becomes cleaner thanks to low- and no-carbon alternatives. [34]

- **Reduce costs**

  Energy storage can reduce grid operating costs and save money for electricity consumers who install it in their homes and places of business. By storing inexpensive energy and using it later, at higher electricity rates, during peak periods, energy storage can lower the

cost of providing frequency regulation and spinning reserve services as well as offset the costs to customers.

Businesses can avoid expensive interruptions and carry on with regular operations by adopting energy storage during temporary outages. People can protect themselves from wasted food and medication as well as the inconvenience of power outages. Also, when offered, demand response programs are open to participation by both commercial and residential customers.

- **Provide different resources**

  By storing excess energy while the wind is blowing and the sun is shining and releasing it when the reverse is happening, energy storage can smooth out the supply of variable or intermittent resources like wind and solar.

  Storage, however, can also help with the effective distribution of electricity for baseload, rigid resources. Energy storage may inject or extract electricity as needed to precisely match load - anywhere and whenever it is needed - when demand varies quickly and flexibility is required. One such enabling technology is energy storage. Energy storage is a possibility even when the sun isn't shining or the wind isn't blowing. Energy storage can be used when demand changes and baseload supplies are unable to respond quickly enough. [34]

- **Boost Dependability and Resilience**

  During outages, energy storage can offer backup power. The same idea that governs backup power for a single item (for instance, a smoke alarm that plugs into a house but also has battery backup) may be expanded up to backup power for an entire building or even the entire grid.

  Storage gives the grid flexibility so that consumers always have access to power no matter where they are or when they need it. Both reliability and resilience depend on this flexibility. The benefit of improved resilience and reliability also rises as the cost of outages continues to climb.[34]

2.5 Electrolytes

The choice of electrolytes and electrode material affects the performance of a supercapacitor and battery. Electrolyte is a mixture of electrolytic salt and solvent that increases ionic conductivity and facilitates the movement of electrons between the electrodes of a cell. When energy is stored

in an EDLC or a pseudo-capacitor, the electrolytes contribute to the formation of an electrochemical double layer and a reversible redox reaction, respectively [35]. Internal resistance, cycle life, and power/energy density are all affected by the conductivity of the electrolytes, their interactions with one another, the electrode material, and the voltage window of the electrolytes.

There are two groups of SC and battery electrolytes: liquid electrolytes and solid/quasi-solid state electrolytes. Liquid electrolytes consist of aqueous electrolytes, organic electrolytes, and ionic liquids, whereas solid electrolytes consist of organic electrolytes and inorganic electrolytes (ESPW) [36].

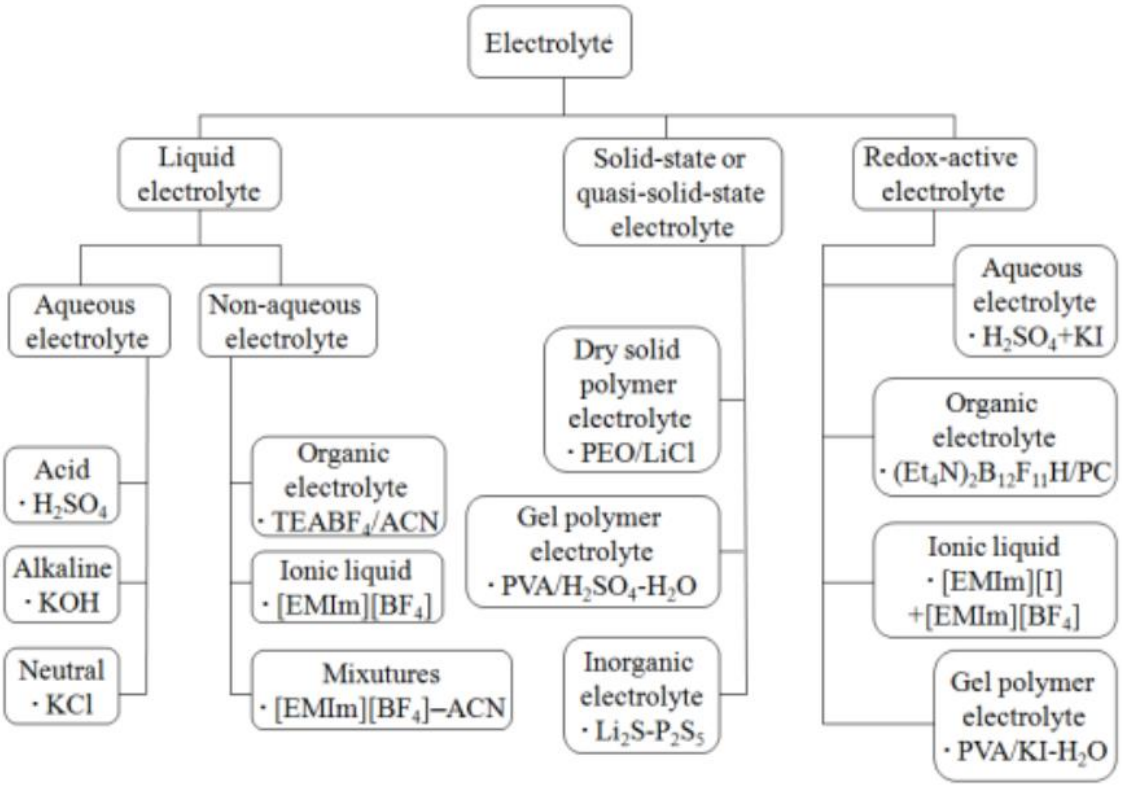


Figure 2. 4 Classification of electrolytes for electrochemical supercapacitors *[35]*

2.5.1 Liquid Electrolyte

2.5.1.1 Aqueous Electrolytes

The most popular liquid electrolytes in electrochemical SC are aqueous electrolytes because of their high conductivity, which is higher than that of organic and ionic liquid electrolytes. The high conductivity of aqueous electrolytes reduces equivalent series resistance (ESR), raising the power density of ESs [36]. Aqueous electrolytes are also affordable and simple to use. Handle as

electrolytes as opposed to organic and ionic liquid electrolytes, which require particular purification in a controlled environment to prevent moisture contamination.

Aqueous electrolytes' primary drawback is their narrow voltage window, which results in SCs with low energy densities [35]. The size of bare and hydrated ions and cations, as well as the mobility of the ions, are the selection criteria for aqueous electrolytes. Ionic conductivity and capacitance value are both impacted by these factors. Acidic aqueous electrolytes are categorized further. Neutral and alkaline solutions, such as H2SO4, KOH, and Na2SO4, respectively [35].

2.5.1.2 Organic Electrolytes

Organic electrolyte-based S Cs are currently dominating the commercial market due to their huge operation potential window, which is typically between 2.5 and 2.8 V. The improved energy and power densities can be brought about by the increased operation cell voltage. In addition, organic electrolytes enable the use of less expensive materials for current package collectors. Tetraethylammonium tetrafluoroborate (TEABF4) and other conductive salts are dissolved in acetonitrile (CAN) or polypropylene carbonate (PC) to create the standard organic electrolytes for commercial EDLCs [35], [37].

However, there are extra factors to consider when using organic electrolytes for SCs. Organic electrolyte-based devices are often more expensive, have a smaller specific capacitance, and a lower conductivity than aqueous electrolyte-based devices. Concerns with safety, such as flammability, volatility, and toxicity, are also present.

In addition, rigorous assembly and purification methods are required for organic electrolytes in a controlled environment in order to eliminate any remaining contaminants (such as water) that could cause considerable performance degradation and problematic self-discharge. Similar to aqueous, the parameters of salts and solvents, including ion size, ion-solvent interaction, conductivity, viscosity, and ESPW, have a substantial effect on the performance of organic electrolyte-based supercapacitors [35], [37].

2.5.1.3 Ionic Liquid Electrolytes

The melting of salts produces ionic liquid electrolytes in order to balance lattice energy. They contain cations and anions with melting points below 1000 degrees Celsius. They possess high thermal and chemical stability. The ratio of cations to anions influences its combustibility [35]. It is more expensive and has a poorer ionic conductivity than water-based electrolytes [4].

2.5.2 Solid/quasi-solid-state electrolytes

Due to the rapid growth in power for portable electronics and the reduction in size of electronic devices, solid-state electrolytes have become an essential topic of study. Solid-state electrolytes, unlike the majority of liquid-based electrolytes, can act as both electrode separators and ionic conducting media. Solid-state electrolytes significantly simplify the packaging and production of SCs, and eliminate the risk of liquid leakage. Polymer-based solid-state electrolytes and inorganic solid-state electrolytes, such as ceramic, are the two most common forms of solid-state electrolytes utilized in the production of SCs. [35].

2.5.2.1 Polymer-based solid electrolytes

The solid polymer electrolytes and gel polymer electrolytes are the two major kinds of solid polymer electrolytes. Gel polymer electrolytes (GPE) are also known as quasi-solid-state electrolytes due to the presence of the liquid phase. GPE is composed of polymer hosts and an aqueous electrolyte such as H2SO4 or a solution of conducting salt in a solvent. In GPE, the solvent can expand the polymer matrix, and ions migrate to the solvent phase instead of the polymer phase.

Due to the liquid phase, GPEs have a higher conductivity than solid polymer electrolytes, which is advantageous. Low mechanical strength, which can lead to internal short circuits, and a limited operating temperature range, especially when water is the solvent, are disadvantages of GPEs. GPEs contain polymer matrix materials such as polyvinyl alcohol (PVA), polyacrylic acid (PAA), potassium polyacrylate (PAAK), poly (ethyl oxide) (PEO), poly-(methyl methacrylate) (PMMA), and poly(ether ether ketone) (PEEK). The solid polymer electrolyte (SPE), often known as a dry electrolyte, consists of a salt such as LiCl and a polymer such as PEO. The passage of salt ions through the polymer [35] contributes to the ionic conductivity of SPE.

2.5.2.2 Inorganic solid-state electrolytes

In general, inorganic solid-state electrolytes for SCs are thermally stable and mechanically reliable. Li2S-P2S5 glass-ceramic is an example of an inorganic solid electrolyte that serves as both an ion conductor and a separator for all solid-state SCs. CNT is added to the electrode material as a particular capacitance to increase the interfacial contact between the electrode material and the electrolytes [35].

2.6 Conducting Polymers

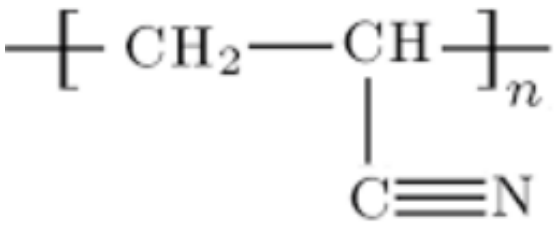
They are organic polymers that are electrically conductive. [38], [39] These substances may be semiconductors or metallic conductors. The ability of conductive polymers to be handled, mostly

by dispersion, is their primary advantage. Conductive polymers cannot be thermoformed because they are not necessarily thermoplastics. They are, nonetheless, organic compounds, similar to insulating polymers. They have great electrical conductivity but lack the mechanical characteristics of other widely available polymers. Advanced dispersion techniques and chemical synthesis procedures [40] can be used to fine-tune the electrical characteristics [41]. Common conducting polymers include polyacetylene, PPy, polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT), and PANI.

2.7 Polyacrylonitrile (PAN)

A synthetic resin produced from the polymerization of acrylonitrile. Belonging to the key family of acrylic resins, it is a thermoplastic substance that is resistant to the majority of solvents and chemicals and is solid and hard. Poor gas permeability and low combustion rate. The majority of polyacrylonitrile is manufactured as acrylic and modacrylic fiber, which is frequently substituted for wool in garments and home décor.

Propylene (CH2=CHCH3) is produced when acrylonitrile (CH2=CHCN) is synthesized from ammonia (NH3), oxygen, and catalysts. Because it is carcinogenic and extremely lethal if ingested, this flammable liquid must be handled and disposed of according to stringent guidelines. Monomers (single-unit molecules) of acrylonitrile are suspended in water as tiny droplets, nearly always in conjunction with other monomers. Free radical initiators subsequently polymerize the monomers into PAN. The polymer's acrylonitrile repeating unit is produced as follows:

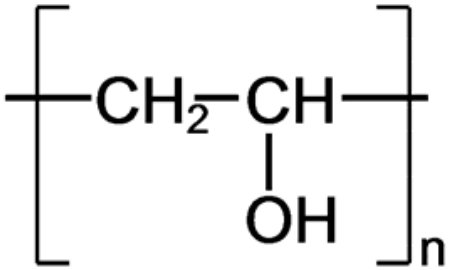


The harmful characteristics of the monomer are absent in PAN. Due to the formation of strong chemical bonds by the nitrile (CN) groups, polymer molecules are resistant to the majority of organic solvents and do not melt without deteriorating. Before being spun into acrylic fibers, which are fibers containing at least 85 percent PAN, the polymer is often dissolved in specialized solvents. Due to the fact that PAN is difficult to degrade and has a strong resilience to coloration, it is employed to generate very little fiber. A copolymer comprising between 2 and 7 percent of a

vinyl comonomer, such as vinyl acetate, can be solution spun into fibers that soften enough to allow dye penetration. Because acrylic fibers are adaptable and flexible, they produce yarns that are airy and lightweight. Acrylics are widely substituted for wool in carpets and clothing, such as knitted socks and sweaters, because to these qualities. Acrylics can be marketed at a tenth of the price of natural fibers since they are more resistant to sunshine, mildew, and moth infestation. Acrylic fibers serve as precursors in the production of carbon and graphite fibers and as a replacement for asbestos in cement, industrial filters, and battery separators.

2.8 Polyvinyl Alcohol (PVA)

Polyvinyl alcohol is a synthetic or manufactured polymer. The molecule of the polymer PVA contains alcohol and vinyl groups. Due to its adhesive properties, this polymer is highly valuable. PVA is naturally crystalline, flammable, and water-soluble. Due to the presence of the alcohol group, it is flammable. PVA differs from other polymers in that it is not produced by polymerizing monomeric precursor molecules, which are tiny, single-unit molecules. Polymers are huge, multi-unit molecule-based chemical substances. Polyvinyl acetate (PVAc), an alternative polymer, is dissolved in an alcohol such as methanol and treated with an alkaline catalyst such as sodium hydroxide in order to make PVA. The acetate groups of the PVAc molecules are removed during the subsequent hydrolysis, also known as "alcoholysis," without altering the long-chain structure. The chemical makeup of the generated vinyl alcohol repeating units is as follows:



The reaction's end product is highly soluble in water but practically insoluble in almost all organic solvents. Incomplete acetate group removal leads in resins that are more soluble in some organic liquids and less soluble in water. PVA is a sizing agent that strengthens textile fibers and improves paper's resistance to oil and grease. It is also utilized as a precursor for the production of other resins, as a water-soluble protective film, and as a component in adhesives and emulsifiers. PVA may be converted into the resins polyvinyl butyral (PVB) and polyvinyl formal (PVB) by reacting it with butyraldehyde ($CH_3CH_2CH_2CHO$) and formaldehyde (CHO) (PVF). Frequently, laminated

safety glass is manufactured with PVB, a durable, transparent, water-resistant, adhesive plastic sheet used primarily in automobiles. PVF is applied for wire insulation.

2.9 Composite Polymer Electrolytes

Composite polymer electrolyte is a polymer matrix with chemically inert inorganic fillers with a high dielectric constant to increase ion conductivity by inhibiting the formation of ion pairs in the polymer matrix. [42] These fillers are frequently made of ceramic. Each of these ceramic fillers is brittle and has a poor dielectric permittivity. It has been demonstrated that mixing polymer electrolytes with an inorganic filler results in a composite material with superior properties to the sum of the parts. [42], [43] A blend of ceramic materials has been shown to increase the ion mobility and conductivity of polymer electrolytes, despite the normally limited ion conduction in polymer electrolytes (in comparison to liquid and solid-state electrolytes). In addition, the polymer's desirable properties, specifically its mechanical strength, are preserved [42].

2.10 Aluminum oxide ($Al_2O_{3)}$

Aluminum oxide, also called alumina, is an amphoteric oxide with the chemical formula Al2O3 (Al2O3). Numerous additional names, including corundum, emery, sapphire, amethyst, and topaz, attest to the mineral's abundance in nature and industry. Corundum is the most common naturally occurring crystalline form of aluminum oxide. Due to trace impurities, the gem-quality variants of corundum, rubies and sapphires, have their characteristic colors. The intense red hue and laser-like capabilities of rubies are due to trace amounts of chromium. Due to impurities such as iron and titanium, sapphires are available in a range of hues. Due to its high melting point and hardness, it is also employed as a refractory material and an abrasive. However, its primary usage is in the production of aluminum metal.

The primary aluminum resource, bauxite, is composed of various minerals, including gibbsite (Al(OH)3), boehmite (-AlO(OH), and diaspore (AlO(OH), as well as iron oxides, quartz, and silicate impurities. Bauxite is utilized extensively in the production of aluminum oxide. Bauxite is purified via the Bayer process, the primary industrial refining method. Bauxite contains just 40 to 50 percent alumina, thus the remainder has been extracted. The remaining insoluble bauxite compounds are filtered out; normally, the wastes result in a red sludge that is difficult to dispose of since it contains arsenic and cadmium. The solution is subsequently cooled, resulting in the creation of a fluffy solid (aluminum hydroxide). The aluminum hydroxide is then heated to 1050 °C, which causes it to separate into aluminum oxide and water.

Despite being an electrical insulator, the thermal conductivity of aluminum oxide is unusually high for a ceramic material (30 Wm1K). Therefore, it is utilized as an insulating material in power electronics. Aluminum's resistance to weathering is attributable to aluminum oxide. Due to the high reactivity of metallic aluminum with atmospheric oxygen, exposed surfaces of the metal form a thin passivation layer of alumina (4 nm in thickness) that prevents further oxidation [44]. This oxide coating can be increased in thickness and properties through the anodizing process.

2.11 Tensile Test

Tensile testing is the assessment of a material's resistance to pressures that pull the sample apart and the extent to which it stretches before breaking. Upon completion of the test, the following characteristics will be determined: Tensile strength at break, ultimate tensile strength, elongation, elongation at break, yield strength, yield strain, young modulus, ductility, and toughness. The following equations are necessary for this test;

$$Area = Width * Thickness \quad ---------- 1.1$$

$$stress = \frac{Force\ (N)}{Area\ (mm^2)} \quad ---------- 1.2$$

$$Strain = \frac{extension\ (\Delta l)}{original\ length\ (l_0)} \quad ---------- 1.3$$

$$Modulus\ of\ Elasticity = \frac{Stress}{Strain} \quad ---------- 1.4$$

$$Area\ under\ the\ curve = \frac{E\varepsilon_R^2}{2} \quad ---------- 1.5$$

2.12 Nano-indentation Technique

Nano-indentation is a nondestructive technique for characterizing the mechanical reaction of materials. It produces nano-sized depressions less than 200 nm (based on ISO 14577-1). Because conventional mechanical and tribological testing methods, such as the tensile test, cannot effectively reflect the mechanical and tribological features of thin films, it is also largely used for thin films. In addition, nano indentation yields characterization results devoid of substrate damage and delamination. In addition, it can be used to describe materials in bulk. Hardness, yield strength, strain hardening coefficient, fracture toughness, and viscoelastic qualities are among the mechanical parameters of bulk materials that are commonly measured using this technique.

2.13 Mechanical Properties of Polymer Based Solid Electrolytes

Kingsley Orisekeh et al. [45] developed solid polymer blend electrolytes based on PVA/PVP. The solid polymer blend was made by dissolving 0.5 g of PVA and 0.5 g of PVP in 25 g of distilled water, each constituting 2 wt% of the solution, and changing the concentration of the lithium perchlorate with 1, 2, 3, 4, and 5 wt%. The SEM, XRD, and FTIR were used to characterize the various compositions produced, and it was discovered that the dissolution of salt (LiClO4) in the blend polymer film causes an increase in the uniform roughness of the film surfaces. Crystallites are also seen in some mix polymers as the salt content increases. The XRD data also show that the PVA/PVP is amorphous in nature, which is extremely clear. They also suspended the samples for mechanical tests such as tensile, fracture toughness, and nano indentation, and discovered that as the concentration of salt (LiClO4) in the blends increased, so did the hardness, young modulus, and fracture toughness, reaching an ideal value of PVA/PVP/4% LiClO4, after which the properties decreased. The tensile strength of the PVA/PVP mixture is higher than that of the various LiClO4 salt concentrations.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Materials

The analytical grade chemicals and reagents were used immediately after delivery, with no additional processing. Aluminium Oxide (Al2O3) powder, PVA pellet with Mw 85,000-124,000 g/mol (99+% hydrolyzed), and PAN pellet with Mw 150,000 g/mol. Dimethyl sulfoxide (DMSO) was used to prepare the sample.

3.2 The process of creating the solid polymer blend

Six (6) different polymer electrolyte films of varying compositions were produced. The samples were identified using the letters A, B, C, D, E, and F. 0.4625g of PVA was dissolved in 15ml of Dimethyl sulfoxide (DMSO) and constantly stirred at 300 rpm for 2 h at an 80oC heating temperature. The mixture was then stirred continuously at the same temperature while 0.075g of PAN and x grams of aluminum oxide (0, 0.0054, 0.016, 0.027, 0.038, and 0.054) were added.

In a beaker, dimethyl sulfoxide was measured first, and then the required amount of PVA precursor was added. Considering the fact that PAN can only dissolve in polar solvents, dimethyl sulfoxide was selected as the best solvent for polymer dissolution. The solution was then transferred into a polypropylene petri dish (tefflon) and dried in a vacuum oven at 60°C. Free-standing films of varied compositions were created after the solvent had entirely evaporated. The resulting flexible, homogenous films were stored in a desiccator for subsequent characterization; Figure 1 presents one of the films.

3.3 Materials Characterization

3.3.1 Fourier Transform Infra-Red Resonance (FTIR) spectroscopy

Fourier transform infrared resonance spectroscopy on gel polymer electrolyte samples was performed using a Thermo Scientific Nicolet iS5 spectrometer with a wavenumber range of 500 to 4000 cm^{-1}.

3.4 Mechanical Properties Test

3.4.1 Tensile Test

Tensile testing was performed on both the pure and doped PVA-PAN films using the Instron 8872 Servohydrolic Tensile Tester, which is produced by Instron and is based in Norwood, Massachusetts. Tensile testing was performed on dog-bone specimens (Figure 2) at a crosshead speed corresponding to a strain rate of 4 x 10-2 s^{-1}.

3.4.2 Nanoindentation analysis

The homogeneous, flexible films were placed on a steel stage for the indentation test. Indentation studies were used to estimate the Young's and hardness values of the SSE (PVA/PAN/Al_2O_3 moduli). The resulting films had an average thickness of 0.15 mm when measured using a micrometer screw gauge. The TI950 Triboindenter (Hysitron Inc., Minneapolis, MN) was used in conjunction with a Dimension 3100 scanning probe microscope (Veeco Instruments Inc., Woodbury, NY) to measure the indentation on all of the prepared films while keeping the relative humidity below 5% to prevent the film from absorbing moisture from the environment. A Berkovich indenter tip, a three-sided pyramidal tip with a 142.3 included angle.

The indentation loading profile included three actions: loading to a peak load in 10 seconds, retaining the peak load for 5 seconds, and loading back to zero in 10 seconds. Peak loads ranging from 500 to 1000 N were used. The sample's average elastic modulus and hardness were calculated using grid indentation with multi-points and a 6 x 6 (36-point array) matrix mapping. Every experiment in the grid uses the same load function. To prevent potential interactions between adjacent indents, all of the indents were separated by at least 7 m. A contact-based scanning probe approach was used to photograph the surfaces before and after the indentation.

In general, surface roughness levels were significantly lower than indentation depths. To mitigate the effects of rough surfaces, indentation depths for metallic materials should be at least 20 times greater than the average surface roughness [46]. Furthermore, to limit substrate impacts, indentation depths should be less than 10% of the film thickness19, especially for tougher films than the substrate. This inquiry used a variety of peak pressures that produced a range of contact depths during the indentation experiments to evaluate any potential consequences of indentation depth. Last but not least, the peak loads were held constant for a long enough period of time to limit the effects of viscoelasticity on the measured elastic moduli.

Loads above the peak values were applied to the samples to determine fracture toughness, in addition to evaluating the elastic modulus and hardness. The Triboindenter was outfitted with a scanning probe microscope (SPM) for viewing sample pictures.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Fourier Transform Infra-red (FTIR) Resonance

In Figure 4.1, the FTIR transmission spectra of pure PVA/PAN and PVA/PAN-based solid polymer films with varying Al_2O_3 concentrations are displayed. It is believed that the band at 2245 cm^{-1}, which comes from PAN, is caused by the characteristic vibration of nitrile (C≡N) bonds, proving the presence of the nitrile group in the polyacrylonitrile chain. According to the literature [47], [48], the hydroxyl group's - OH stretching vibration causes the transmission band of pure PVA to fall between the values of 3500 and 3200 cm^{-1}. The polymer blend's respective IR bands at 2932, 1652, 1424, and 1041cm^{-1} are caused, respectively, by (C-H)n asym-metric stretching, C-O stretching, CH_2 bending, and C-O stretching [47]. As Al_2O_3 was added to the polymer blend, the peaks increased; however, they started to decline once there were 10 weight percent of Al_2O_3 nanoparticles present. The interaction of the polymer blend with Al_2O_3 nanoparticles in the PVA/PAN/ Al_2O_3 based solid polymer electrolytes is indicated by the shifting and disappearance of the bands, as well as the production of new bands in the electrolytes.

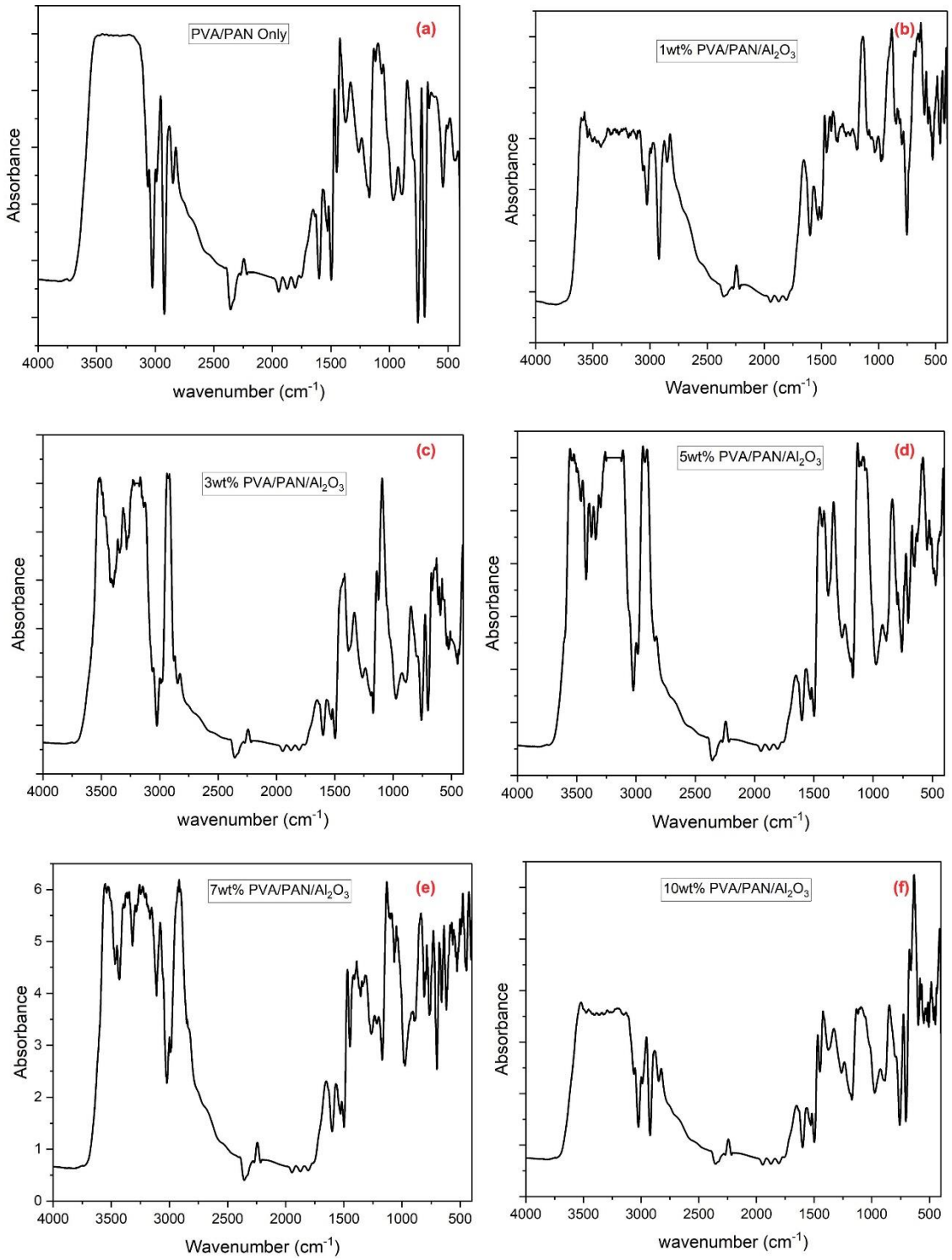


Figure 4. 1 FTIR spectra of the samples **(a)** Pure PVA/PAN **(b)** 1 wt% PVA/PAN/Al2O3 **(c)** 3 wt% PVA/PAN/Al2O3 **(d)** 5 wt% PVA/PAN/Al2O3 **(e)** 7 wt% PVA/PAN/Al2O3 **(f)** 10 wt% PVA/PAN/Al2O3

4.2 Tensile Test

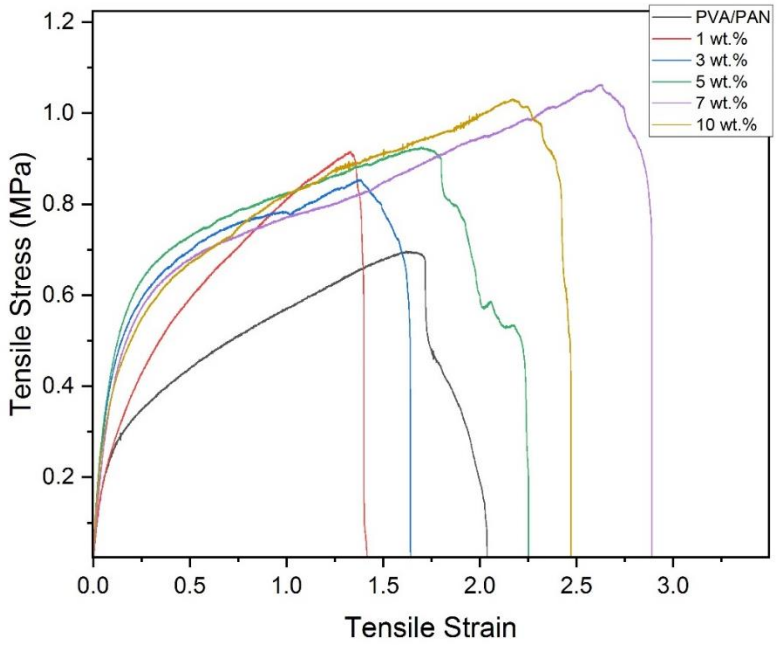


Figure 4. 2 Tensile stress (MPa) versus tensile strain curve for all the samples

Figure 4.2 indicates that prior to necking (plate 4.2a) happening at the maximum point of each sample, all samples undergo both elastic and plastic deformation. As the load is applied, micro voids form, expand, and eventually merge across the necking region of the specimen gauge length.

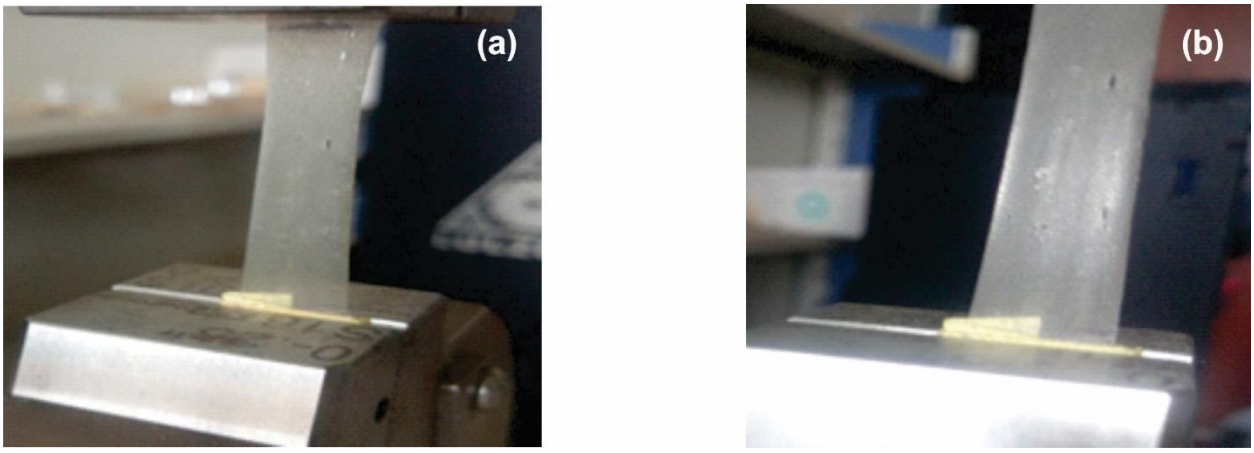


Plate 4. 1 Crack initiation as the sample is exposed to tensile loading

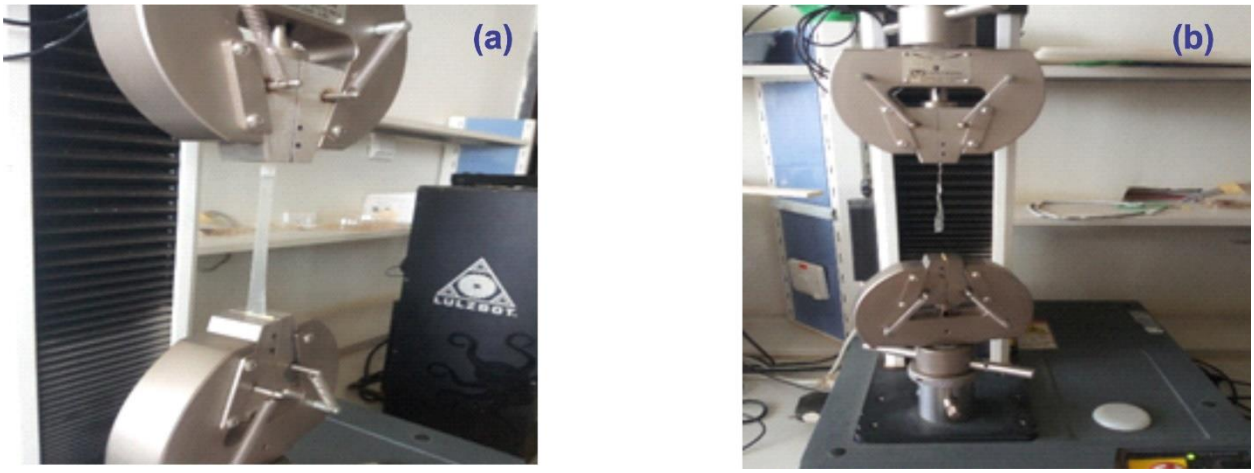


Plate 4. 2 (a) Necking (b) Failure of the sample

This causes a crack with a plane perpendicular to the imposed tensile stress, which spreads as the material is further stressed until it fails (plate 4.2b). The mechanical parameters of each sample, as calculated from the results of tensile testing and the stress-strain curve in Figure 4.1, are listed in

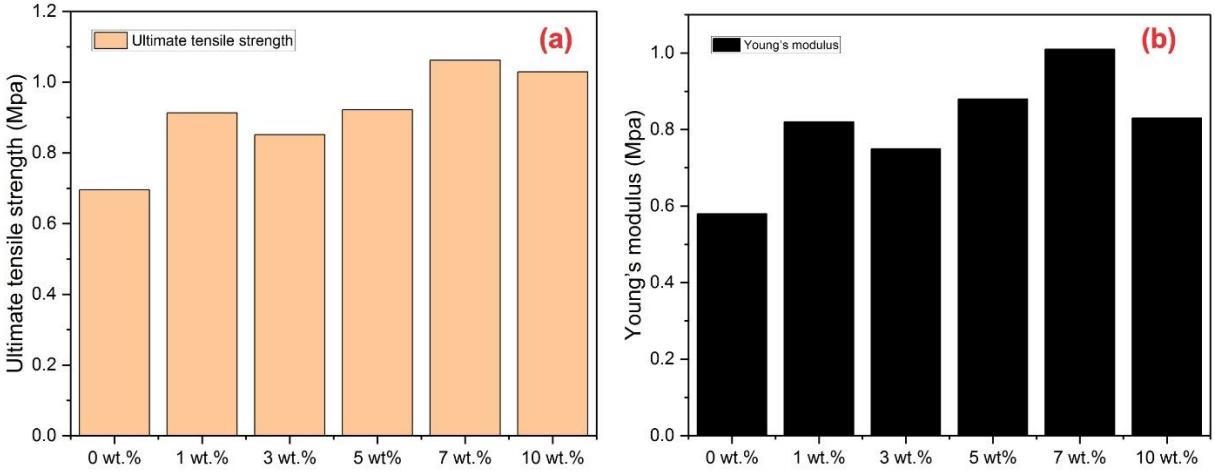


Figure 4. 3 Representation for the samples (a) Ultimate tensile test (b) Young modulus

As the percentage of aluminum oxide particles increases from 0% to 7%, the tensile strength and the young modulus also increase. In addition, the material containing 10 percent by weight of aluminum oxide nanoparticles demonstrates a slight decrease in tensile strength and young modulus. Figure 4.3 (a) and (b) demonstrate that the tensile strength of the PVA/PAN/Al_2O_3 tends to decrease initially at 3 wt%, but as the composition of Al_2O_3 increases, there is a gradual increase

in both the tensile strength and the young modulus until it reaches 7 wt% of the aluminium oxide nano particles, which is the optimal composition of all the samples tested.

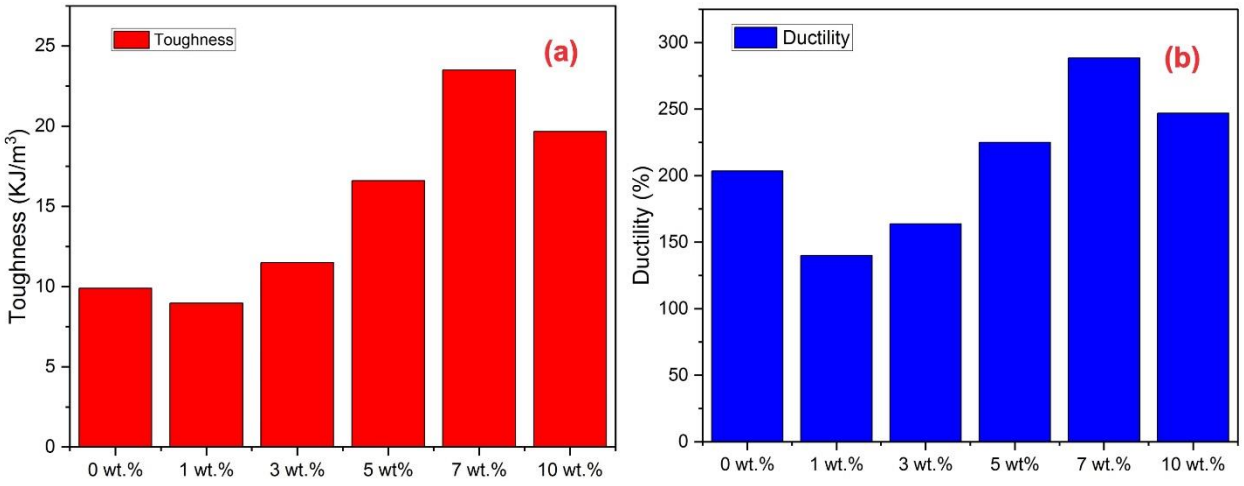


Figure 4. 4 Representation for the samples (a) Toughness (b) Ductility

All PVA/PAN/ Al_2O_3-generated compositions exhibited % Elongation values within the range of 139.9% to 288.4%. There is no visible pattern in the accumulation of nanoparticles of aluminum oxide in the sample. Considering that the ductility and toughness of PVA/PAN/Al_2O_3 generally decrease as the percentage of Al_2O_3 nanoparticles increases, then increase as the percentage of nanoparticles approaches 3wt%, reaching an ideal composition of 7wt%. Figure 4.4(b) demonstrates that the compositions containing 5wt%, 7wt%, and 10wt% of aluminum oxide nanoparticles had greater average percent elongation values than the other series developed, with 7wt% PVA/PAN/Al2O3 being the best composition. The results reveal that the inclusion of nanoparticles of aluminum oxide increases the ductility of PVA/PAN.

The tensile strength of each PVA/PAN/Al2O3 mixture is depicted in Fig. 4.4 (a) and determined using Eq. 1.6. This composition contains values of 9.9, 8.97, 11.5, 16.6, 23.5, and 19.66 KJ/m3, which correspond to zero weight percent, one weight percent, three weight percent, five weight percent, seven weight percent, and ten weight percent, respectively. The huge discrepancies between these values indicate that the toughness of PVA/PAN/Al2O3 increases with the amount of nanoparticles present, reaching an optimal value at 23.5 KJ/m3 or 7 weight percent of aluminum oxide nanoparticles present in PVA-based electrolytes.

Table 4. 1 Tensile properties for all samples

	Ultimate tensile strength (MPa)	Young's modulus (Mpa)	Stress at break (MPa)	Ductility (%)	Toughness (KJ/m^3)
PVA/PAN only	0.695	0.58	0.09	203.6	9.9
1wt% of PVA/PAN/Al_2O_3	0.913	0.82	0.10	139.9	8.97
3wt% of PVA/PAN/Al_2O_3	0.851	0.75	0.52	163.8	11.5
5wt% of PVA/PAN/Al_2O_3	0.922	0.88	0.22	225.1	16.6
7wt% of PVA/PAN/Al_2O_3	1.062	1.01	0.67	288.4	23.5
10wt% of PVA/PAN/Al_2O_3	1.029	0.83	0.43	247	19.66

These results suggest that the characteristics of these samples differ from one another. Table 4.1 shows that the ultimate tensile strength (UTS) of each sample varied. In the same way that complex samples have greater young moduli, pure PVA/PAN samples have lower young moduli, with the highest value being 1.01Mpa for a 7wt% PVA/PAN/Al_2O_3 sample. As the concentration of oxide particles increases, stronger bonds between the polymer matrix and Al_2O_3 particles develop. However, the decrease in the young modulus and ductility values indicates that the composite material becomes brittle when its Al_2O_3 particle concentration exceeds the optimal value.

4.3 NANO-INDENTATION

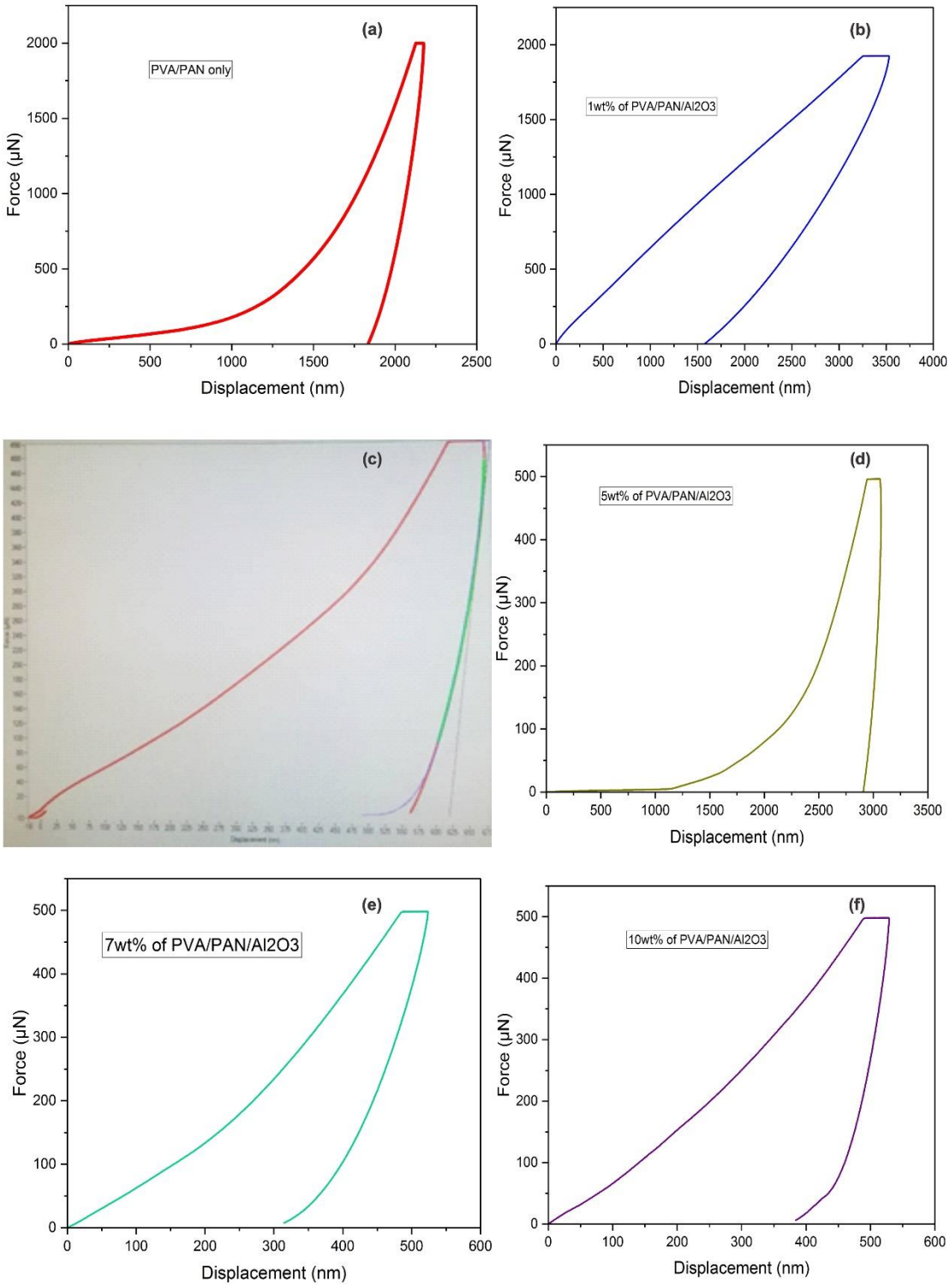


Figure 4. 5 Force-displacement curve for the samples from Nano indentation test **(a)** PVA/PAN only **(b)** 1 wt% PVA/PAN/Al2O3 **(c)** 3 wt% PVA/PAN/Al2O3 **(d)** 5 wt% PVA/PAN/Al2O3 **(e)** 7 wt% PVA/PAN/Al2O3 **(f)** 10 wt% PVA/PAN/Al2O3

The results obtained for the Hardness and decreased modulus in Figure 4.5 are summarized in Figure 4.6, and the mechanical properties of the generated composites are shown in Table 4.2. Prior to hardness and stiffness tend to increase with increasing Al_2O_3 nanoparticle content, it was noticed that the hardness and reduced modulus of the polymer blend were dramatically decreased when Al_2O_3 nanoparticles were initially introduced.

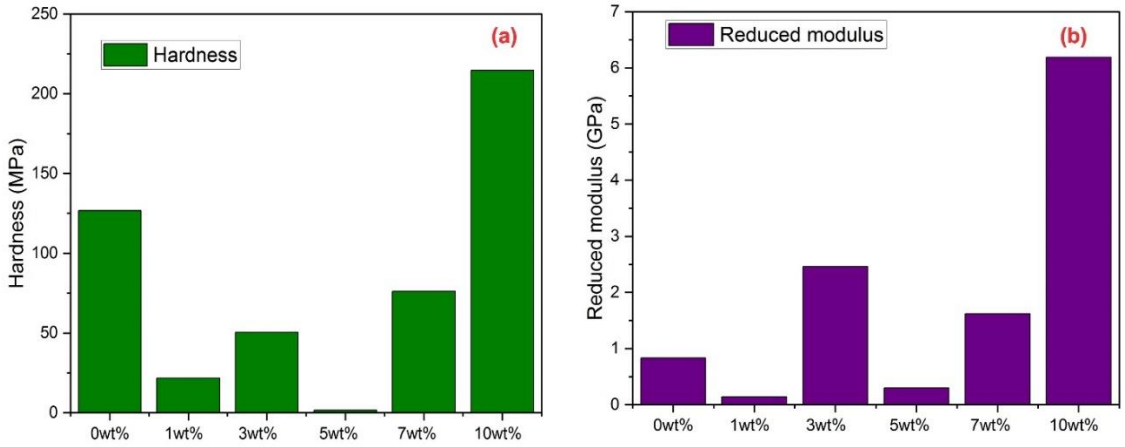


Figure 4. 6 Representation for the samples (a) Hardness (b) Reduced Modulus

This significant decrease in hardness and the reduced modulus value may be the result of poor adhesion at the blend interface at 1wt% and 5wt% Oxide particle concentrations in the Polymer blend. In contrast to the tensile strength, which reached its peak at a concentration of 7wt% Al_2O_3, the hardness and the reduced modulus value increased, reaching their highest value at a concentration of 10wt% Al_2O_3 (214.71 MPa and 6.19 GPa, respectively), which explains the slight decrease in tensile strength at the same composition (Table 4.2).

Table 4. 2 Indentation tests result for the PVA/PVP/Al2O3 at different Aluminium oxide nanoparticles concentration

	Hardness (MPa)	Reduced modulus (GPa)
PVA/PAN only	126.70	0.833
1wt% of PVA/PAN/Al_2O_3	21.86	0.139
3wt% of PVA/PAN/Al_2O_3	50.52	2.46
5wt% of PVA/PAN/Al_2O_3	1.62	0.299
7wt% of PVA/PAN/Al_2O_3	76.11	1.62
10wt% of PVA/PAN/Al_2O_3	214.71	6.19

There is also evidence that voids formed in Plate 4.1 and combined to generate enormous fissures. Trends in the measured Young's moduli and hardness values also show that designing robust films with suitable blends of strength, Young's modulus, and ductility can be achieved by controlling the blend ratios.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This research study has shown a simple method to optimize the amount of Al_2O_3 nanoparticles in the polymer based solid electrolyte, hence improving the mechanical properties of PVA/PAN based solid electrolyte. By dissolving PVA/PAN in DMSO and adding the Al2O3 to the mixture then drying in a vacuum oven, six (6) distinct polymer electrolyte films with varied compositions were produced. To explore the behaviors of the generated flexible thin film, FTIR, tensile testing, and nano-indentation were used. With a tensile strength of 1.062 MPa, a young's modulus of 1.01 MPa, a ductility of 288.4%, and a toughness of 23.5 KJ/m3, 7 wt.% Al_2O_3 was found to be the best composition among all samples. The polymer-based matrix containing 10 wt.% Al_2O_3 nanoparticles, however, exhibits the highest values of hardness and reduced modulus, measuring 214.71 MPa and 6.19 GPa, respectively. According to the experiment results, the Al_2O_3 nanoparticles being added to the mixture significantly improve the mechanical properties of the PVA/PAN polymer based solid electrolyte.

5.2 RECCOMENDATION (S)

The scope of this work is to explore the possibility of an optimum amount of Al_2O_3 that can be used as reinforcement in the polymer based solid electrolyte. In the process of characterization of the polymer based solid electrolyte, only the Fourier Transform Infra-Red Resonance spectroscopy (FTIR) was employed. further characterization techniques such as X-ray diffraction techniques should be done to understand the crystalline nature of the electrolyte, and scanning electron microscopy (SEM) to comprehend the microstructural configuration of the electrolyte material. Mechanical test like fracture toughness should also be done to understand behavior of the polymer based solid electrolyte when crack is initiated. In addition, Attempts and further research could be geared towards the electrochemical characterizations of the polymer based solid electrolyte.

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