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Production and Characterization of Polyurethane Fibers by Forcespinning Method and Incorporation of Luminiscense Nanoparticles

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PRODUCTION AND CHARACTERIZATION OF POLYURETHANE FIBERS BY

FORCESPINNING METHOD AND INCORPORATION OF LUMINISCENSE

NANOPARTICLES

A Thesis

by

SUNANDA KUMAR SAHA

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ABSTRACT

Saha, Sunanda K, <u>Production and Characterization of Polyurethane Fibers by Forcespinning Method and Incorporation of Luminescence Nanoparticles</u>, Master of Science Engineering (MSE), August, 2021, 93 pp., 2 tables, 23 figures, references, 76 titles.

In this work, Polyurethane (PU) fine fiber nonwoven mats are generated using the Forcespinning® method. A detailed study focusing on the effect of PU concentration within solutions of N, N Dimethylformamide and the effect of relative humidity (RH) on fiber average diameter and fiber yield is presented. Solutions were prepared with 4 different concentrations, 14, 15, 16 and 17 wt% of PU. It was observed that as concentration of PU increases, average diameter shows a tendency to increase. Production of fibers with RH varying from 30RH to 60RH was analyzed. Fiber Production is optimized in terms of concentration and rpm. Fibers were characterized under a scanning electron microscope to evaluate fiber size and surface features and their thermal characteristics were evaluated with DSC (Differential scanning calorimetry) and TGA (Thermogravimetric analysis). Contact Angle measurements were also performed revealing it's hydrophobicity. Further, Mn doped Zn_2GeO_4 and Cr doped $ZnGa_2O_4$ nanoparticles which are capable of providing green and red emission under UV light were synthesized, then characterized with XRD and PL Spectroscopy. The particles are attempted to integrate with the produced fiber mat, among 3 attempted strategy, scratching with a card over Al foil, nanoparticles sticking with it, gives comparatively a better result.

DEDICATION

All praise to almighty GOD, without His blessings I won't be able to make it until this point. I want to dedicate this work to my parents, who have always showed me their love, and support from my home country; for their encouragements, sacrifice, compassion, mental support, and love; also, my sibling, Sanat Saha love and affection.

ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

Main Objective

Development of smart textiles through the production of PU nanofibers via Forcespinning.

Smart textiles will be developed by incorporating specifically designed nanostructures

Detailed Objectives

1. Produce Nanofibers using DMF(Polymer Precursor) via Forcespinning

2. Optimizing Nanofiber production to create fiber mat

3. Fiber morphology analysis for the evaluation of it's nanoscale

4. Thermal properties and hydrophobicity/hydrophilicity check.

5. Substantial Method for nanoparticles synthetization a) Mn doped Zinc Germanate (Mn: Zn_2GeO_4) Nanorods (Green) Biphasic b) Cr doped Zinc Gallate (Cr: $ZnGa_2O_4$) Nanoparticles (Red) Biphasic c) Zinc Gallo- Germanate (Zn_2GeO_4) Nanosheets (White) Biphasic

6.Incorporate them into nanofiber

7. Characterization of nanoparticles and resultant nanofiber

Thesis Structure

The Chapter 1 discusses the background, motivation, and significance of this project.

Chapter 2 is a review of the literature focusing primarily on Polyurethane fiber production and it's composite with nanoparticles.

 Chapter 3 takes and explains techniques to produce fiber and it's characterization.

Chapter 4 takes fiber nanoparticle synthetization technique and it's characterization.

The results of the study are exposed and discussed in chapter 5

Chapter 6 is the conclusion of the project.

CHAPTER II

REVIEW OF LITERATURE

Textile Industry

Textiles is one of the most impactfule and influential among the substantial desires of human life. The textile industry processes fibers into yarn, transforms the yarn into fabrics or useful commodities, and dye and finish these materials through diverse operations of production. Numerous dyes, chemicals, auxiliary chemicals, and sizing materials are used during wet processing in the textile industry.The global textile industry impacts nearly every human being on the planet. The industry is currently worth nearly US $3 trillion and includes the production, refinement, and sale of both synthetic and natural fibers used in thousands of industries. As you can see, the textile industry encompasses an eclectic range of products with an even broader range of applications. That diversity is one of many factors that makes the textile industry one of the most crucial to world ecomony . It is estimated anywhere between 20 million and 60 million people are affiliated with the textile industry worldwide. Employment in the garment industry is particularly important in developing economies and helping them to improve their conditions. The industry has share of approximately 2% of global Gross Domestic Product and accounts for an even greater portion of GDP for the world's leading producers and exporters of textiles and garments. The textile industry comprises with many sectors that fabricate and/or process textile-associated commodities (e.g., fibers, yarn, and fabric) for additional processing into

clothing,household products, and industrial products. Textile industry works with collect and arrange fibers; alter fibers into yarn, thread, or webbing; transform the yarn into fabric or allied commodities; and dye and finish these commodities during the steps involved in textile manufacturing. The textile industry requires a massive amount of dyes, chemicals, and other materials to impart the required qualities to the fabrics which leads to flourish other related industries.

Brief History

The term 'Textile' arrived from the latin word 'texere' which means 'to weave'. Textile product can be attributed to a flexible material comprising of a network of natural or artificial fibers, known as yarn. Textiles are formed by sequence of process such as weaving, knitting, crocheting, knotting and pressing fibers together.

History of Textile The history of textile can be traced very far back of human civilization and as time moves on the history of textile has further enriched itself. In the 6th and 7th century BC, invention of flax and wool fabric at the excavation of Swiss lake inhabitants is considered first found usage of fibers. In India, the culture of silk was introduced in 400AD, while spinning of cotton traces back to 3000BC which were mostly utilized in cloting purposes.

In China, the discovery and development of sericulture and spin silk methods got initiated at 2640 BC . At ancient Egypt the craft of spinning linen and weaving developed in 3400 BC.The discovery of machines and their widespread application in processing natural fibers was a direct outcome of the industrial revolution of the 18th and 19th centuries which was intitaed in Europe. In this cnetury, the discoveries of various synthetic fibers created a wider market for textile products and gradually led to the invention of new and improved sources of natural fiber.The

development of transportation and communication are the prime reason that pave the path of a transaction of varried skills and textile art among various countries

Polymers used in Textile

Polymers are integral parts if the production of textile. Polymers are used in the beginning of textile manufacturing ranging from fiber manufacturing to textile coloration and finishing. Polymer came from the Greek word "poly" and "meros"; poly means many and meros means part [1] Polymers are giant molecules substances made from connection of many small units. These small parts are called monomers. The chemical process where the polymer is formed by the interlinking of many monomers is called polymerization. The polymer synthesized from single monomer is known as a homopolymer such as polyethylene which is formed from ethylene monomer. The polymer created from more than one type of monomers is called copolymer like Polyester is the product of polymerization of two types of monomers—acid and alcohol. Polymerization are primarily two types: Chain and Step Polymerization. In chain polymerization, monomers with double or triple bonds can react without any elimination. In step polymerization, monomers having reactive groups can react with themselves through a stepwise reaction to produce a polymer.

Polymers can be used to produce fiber which is a thread-like substance without any restriction on its chemical composition. Fibers are available in different forms such as metallic, mineral, or organic. All non-metallic fibers are polymeric materials produced abundant in nature or synthesized commercially. Fibers found in nature have been used for long such as cotton, wool, silk. Organic synthetic fibers are mostly thermoplastic however thermosets are also possible. Cotton dominated the textile market until the end of the last century although today most textile products are made of synthetic fibers. The three most important synthetic fibers are polyurethane,

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polyester and acrylic. Many other synthetic polymers are spun into fibers. Of them majority are high performance fibers that are used for textile applications such as bulletproof vests, heat resistant garments, high performance sporting goods, tow cables, etc. Polymers used for synthetic fibers are produced from intermediates and then applying a catalyst. Key catalysts used are manganese, cobalt and antimony oxide to control the processes. Synthetic fibers account for about half of all fiber production, with applications in fiber and textile technology. Four synthetic fibers – nylon, polyester, acrylic and polyolefin – are abundant the market.. Polyester alone accounted for around 80% of the global market share of man made fibers.[2] Polyester has high volume of usage because it can be blended with cotton) in garment production. Polyethylene is considered to be one of the simplest polymer fabricated in textile, it has ethene or ethylene as the monomer whereas the linear polymer is known as the high density polyethylene-HDPE. Many of the polymeric materials have chain-like structures which be similar to polyethylene. Another polymer used in fabrics and textiles for our everyday life is Nylon which belongs to the family of
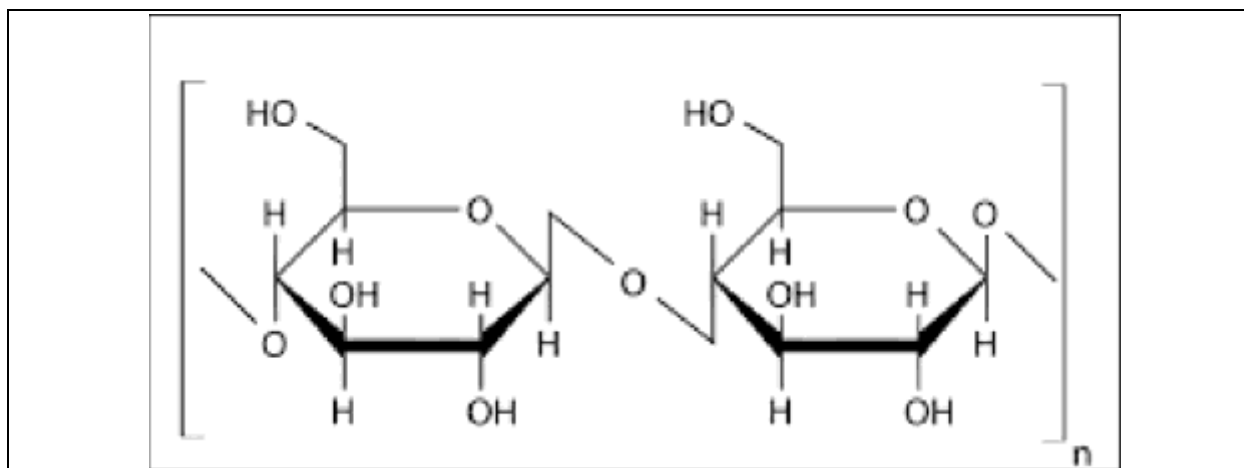
Fig 1: Chemical Structure of Cellulose

Polyamides. Teflon used in non-stick pans, polyvinyl chloride used in pipes. The PET bottles we use are commonly made up of synthetic polymer called as polyethylene terephthalate. The covers and plastic kits comprise synthetic polymers such as polythene. Polyvinyl Chloride or PVC is

third-most majorly produced plastics coming after polypropylene and polyethylene and it is known to be stronger and cheaper than other alternatives. PVC is also used in the clothing, electrical cable insulation including many other applications replacing rubber. Polypropylene also called as polypropene is a kind of thermoplastic synthetic polymer which is used in variety of applications such as textiles and plastics application. Polyurethane is an uprising polymer in textile industry because of it's potential to be used in fabrication of comfortable cloths, sportswear, protective equipment, filtration and medical applications. Therefore, The natural and synthetic fibers being used in constructing the vast majority of staple, decorative and technical textiles are polymeric fibers

Natural Polymer

Cellulose: Cellulose is a linear polymer of 1,4 β glucan, the basis of all plants fibers has a formula of $(C_6H_{10}O_5)_n$ The molecular weight of cellulose varies according to its sources.; For example, cotton cellulose may contain as many as 10,000 glucose units per molecule. Cellulose is formed cotton plant, but mostly combined with lignin and another polysaccharide, called hemicellulose. which is the second available produced polymer available in nature after the cellulose[3]. It is branched-chain non-crystalline low molecular weight polymer with a degree of polymerization of 80–100 and their general formulas are $(C_5H_8O_4)_n$ and $(C_6H_{10}O_5)_n$[4]. Maximum cellulose are available in the plant world. Negligible amount of cellulose is used to produce fine fibers such as cotton. Most of it is used as structural materials of tree such as stems and leaves.

Cotton: Cotton is the most important textile fiber, used to produce apparel and textiles in these industries 40% of fiber consumed is cotton[5]. Cotton is considered as a strong fiber, it's tenacity is 3.0–5.0 g/den. Cotton doesn't stretch easily, it has only 5–10% elongation at break.

Cotton fiber has excellent resistance to heat and doesn't degrade readily and decomposed at 150 °C. Cotton is vulnerable by hot dilute or cold concentrated acids, it's resistance increases with cold concentrated acid and alkalis. Cotton is used widely as a fabric for both hot and cold weather wear. Cotton fibers are able to absorb ample amount of moisture, which makes it comfortable and cool. The moisture absorbance and temperature flexibility make it an excellent candidate to produce sheets, towels, raincoats, carpets and curtains, shoes, clothing, and hats.

Jute: Jute has been used for fiber production in textile industry from ancient time. Jute is a bast fiber composed of 60–70% cellulose, 12–13% hemicellulose, and 12–15% lignin. This fiber is mostly produced in Bangladesh, India, Myanmar, China, Nepal, and Thailand. There are thirty Corchorus species, but only two of them Corchorus capsularis and Corchorus olitorius are
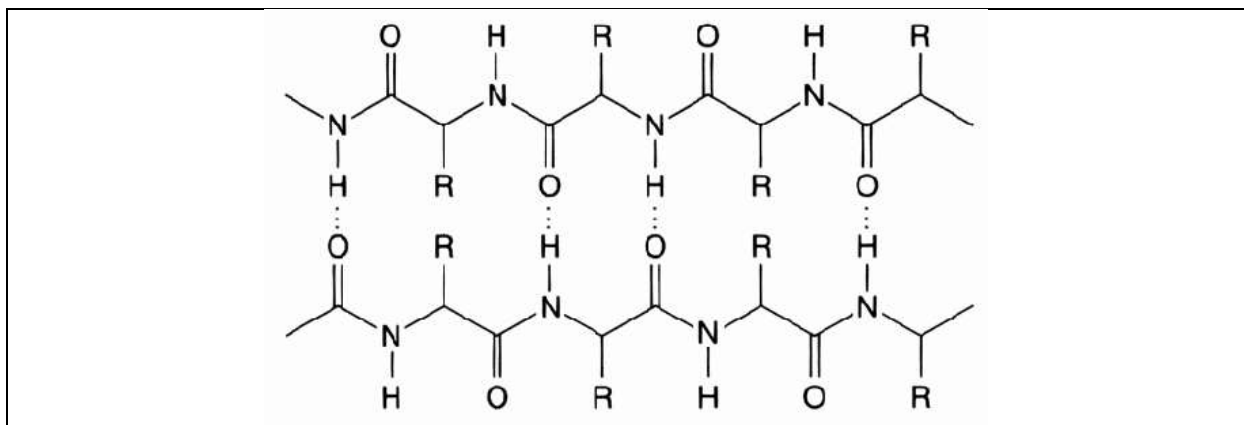
Fig 2:   Fig 2: Keratin from Chicken Feather

worldwide known [6]. Jute is a cheap fiber and due to its strength and availability in large quantity has carried it into making packing clothes, sacks, storage, agricultural products. The fiber has high resistance to elongation. Curtain and furnishing fabrics are also can be made from jute. Presently, jute is commercially blended with cotton fiber for making denim

fabric[6].

Keratin: Keratin is a structural name of proteins, which are outer layer of human skin, in hair, and nails. Keratin has the capability to self-organized into a bundle of fiber. Within the fiber bundle, individual polymer chains are cross-linked with S-S linkage involving the cysteine side Chain [7]. People have developed and processed keratin from animals from old period, e.g., animal skins for protection, different kind of horns, etc. The side groups of the keratin chain may vary size and chemical nature. This side parts can be acidic, basic, hydrophilic, or hydrophobic. Hydrocarbon present in the keratin chain as a side chain is non-polar and hydrophobic. On the other hand, the hydroxyl-containing side chain gives hydrophilic characteristics to the chain. The side chain takes almost 50% of the weight of the polymer. Cystine results in a considerable amount of cross-linking in the fiber and controls significant amount of properties of the polymer[8]

Wool: The wool fiber is composed of keratin. The basic composition of keratin in different types of wool is almost the same, but only the sulfur content differs. This component determines various traits of wool fiber. The tensile strength of wool is in the range of 1,190–230 kg/cm^2 and tenacity of the fiber is of 1.0–1.7 g/den in the dry state, and 0.8–1.6 g/den in wet state. It can be elongated to 25–35% before the break. Wool is resilient in nature due to its excellent elongation at break united with high elastic recovery. Wool can absorb moisture as high as 17%. [9] Wool usually faded with acids, decomposed completely into amino acid by hot concentrated sulfuric acid. It has general resistance to other mineral acids. However, Wool is very sensitive to alkali. Caustic soda can dissolve wool completely. Wool is best known for its warmth. It has been used as clothing for winter such as blanket, jacket, sweaters, cardigans, pullovers, inner garments.

Fibroin: This polymer is an insoluble protein composed of long-chain amino acids basically attached by peptide link with hydrogen bonding [10]. Fibroin is composed of around 87% short-chain amino acid and consists of carbon, oxygen, and nitrogen.

Silk: Silk, the only natural filament, is composed of fibroin protein produced by arthropods. A silk filament contains 72–81% fibroin, 19–28% sericin, 0.8–1.0% fat and wax, and 1.0–1.4% coloring matter and ash of the total weight [11]. Liquid fibroins are extruded by the silkworm from the brins, which unite in the spinneret on its head. Sericin is another protein secreted by the silkworm which attached together liquid fibroins extruded from brins, as a result, a single continuous filament is produced. The filament is thus made by the connection of two brins held together by sericin. [12]. The tenacity of silk filament is usually of 3.5–5.0 g/den. Silk has less strength when gets wet. It loses 15-30% of its' strength upon getting wet. Silk has elongation at break of 20–25% under normal condition and less elastic recovery than wool. Silk shows plasticity, can be permanently stretched if it is drawn about 2% to its original length. Moisture absorbance of silk filament is as high as 11%. Silk is strongly attacked by acids which can disintegrate them into its components amino acid. However, if applied with moderate concentration silk fabric shrinks giving an especial effect known as crêpe. Dilute acids is not very harmful to silk. Silk can also be dissolved in a concentrated caustic solution. In comparison, silk takes relatively more time to be damaged by alkali compared to wool. Silk has been considered as the most astounding natural fibers in nature for past hundreds of years. Silk has been seen as lucrative apparel for a long time due to the combination of high strength, flexibility, good moisture absorption, softness, and luxurious appearance.

Synthetic Polymer

Synthetic fibers are integral part of the textile industry. Synthetic fibers are made of polymers that do not produce naturally and are produced entirely by chemical synthesis in the laboratory or industry. Synthetic fibers are higher in length and are long lasting. Synthetic fibers are made from synthesized polymers of tiny molecules. Many of them are Petroleum

byproducts.[13] There are many different kinds of synthetic fibers; among them polyurethane, polyamide, polyester are widely used. Synthetic fiber's production is on the rise, for example polyester alone surpass the production of most used natural fiber cotton. The fibers of polyvinyl alcohol and polypropylene (PP) are some emerging polymer in regards of their production and usage in textile & apparel. Therefore, research into effective production of these fibers and improving fiber properties is a major concern.

Nonwoven synthetic fabrics are produced by extrusion processes and manufactured cheaply to form disposable products such as polypropylene (PP) and polyester nonwoven fabrics are used in disposable absorbent articles, such as diapers, feminine care products and wipes. Besides, they are also widely used as filtration media, battery separators and geotextiles. To incorporate these features into the fibers, various surface modification and property inclusion techniques are followed. These methods are executed as part of processing to improve various properties such as softness, dyeability, absorbance and wettability. Recent advances in textile chemistry have achieved by research outcome where various functional properties such as antimicrobial activity, decreased skin irritation properties, fragrance property have been imparted. Synthetic fiber is also used in composite industry, three most common synthetic fibers used in composites industries are Kevlar (aramid), carbon, and glass fiber. Synthetic fibers possess about half of all fiber usage, with affiliations in every field of fiber and textile technology as potentially valuable commercial products.

Synthetic fibers are more long-lasting & robust than most natural fibers. In addition, many synthetic fibers offer pragmatic functions such as stretching, waterproofing and stain resistance. Sunlight, moisture, and oils from human skin cause all fibers to break down and wear away in case of natural fibers as it tends to be much more sensitive than synthetic blends. This is obvious

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because natural fibers are biodegradable and biocompatible. Natural fibers are also susceptible to larval insect infestation so synthetic fiber steps up as a remedy.

Most of synthetic fibers' disadvantages are related to their low melting temperature [14] The mono-fibers hardly can capture air pockets like cotton and provide poor insulation. Synthetic fibers have less fire redundancy and susceptible to heat damage. So it melt relatively easily and can be damaged by hot washing. Synthetic fiber generates electrostatic charge by rubbing than with natural fibers. It's not obviously as skin friendly as other natural fibers, so it is uncomfortable for long wearing. These fibers are non-biodegradable so possess some threat for pollution. Most of the synthetic fibers absorb very little moisture so sort of adhesive while body sweats. Even though, synthetic fibers are made from chemicals consisting of superior properties to natural fibers. They are desired in different industries for being profoundly strong and durable, while some dry much quicker than others, or may be more absorbent and easier to dye.

Polyurethane

Polyurethane fibers itself is highly stretch and elastic as rubber, strong than rubber, and resilient to aging. The fiber is very much dyeable and fine yarn can be produced. Polyurethane fiber is manufactured from glycol and diisocyanate as raw material with different spinning methods.

Any commercial polyurethane product is not manufactured with totally poly-urethane fiber. The polyurethane fiber is used by combination with other fibers. In the case a polyurethan fiber is knitted with filament yarn of another polymer, For example, 'Two way tricot' is produced in this way highly elastic both in wale- and course-way and is used for swimsuits, leotards, underwear and other similar stretchable clothing. Covered yarn are also commercially used where

polyurethane is wrapped around with another yearn and used for commercial purposes such as one type used for foundation garments. Where a polyurethane yarn is inserted as a core in the spinning process is referred to as a "core spun yarn". A core spun yarn is used for tights and training wear. Most Polyurethane shows elastic behaviors and they have extension at a break in excess of 200% with rapid recovery when the tension gets released. One such fiber is Spandex which can be defined as "a manufactured fiber in which the fiber forming substance is a long-chain synthetic polymer compromised of at least 85% of segmented polyurethane.[15] Spandex fiber can be spun by melt spinning, dry spinning or wet spinning where Dimethylformamide or DMF is used as a solvent. Melt spun technique is also suitable as its melting temperature is in the range of 175–178°C. It has a density of 1–1.05 g/cc and melting temperature in the range of 175–178°C. Its excellent elongation value can be as high as 700%. One of this fiber's outstanding behavior is elongation at break that generally falls in between 350% and 700% with an elastic recovery of 99% at 200% extension. Though, the elastic modulus is very low and lies in the range of 0.007–0.020 g/day. The fibers are well resistant to alkalis but susceptible to discoloration in acid solution. The fibers can resist peroxide bleaching, ozone, chlorine, and UV radiation. Disperse dye, acid dye and basic dye can be used for coloring this fiber. It has low water absorption capacity. (moisture regain=1.3%). Spandex fiber is most popular among commercial polyurethanes as it can be used as accessories in belts, gloves, socks, tights; in sportswear like swimwear, cycling jersey, apparel for exercise; in apparel like leggings, shorts, skinny jeans, ski pants, yoga pants, brassieres, hosiery, surgical hose, etc. Polyurethane coated fabrics bring great properties as well; they are durable and abrasion-resistant, soft, light and breathable. As such, they are used to create more comfortable and delicate weatherproof clothing such as sports wearing and light rain clothes. Polyurethane coatings are also used for leather-like materials and in fact have similar stretch,

stiffness and permeability properties with less costings. No plasticizers are used in PU upholstery so there is no cracking or peeling, and it remains soft and supple for the duration of time PU fabrics are also easier to decorate.

The chemical structure, physical properties and notable work with Pu fibers will be discussed in a later section of this book.

Polyester

Polyester fiber is defined as a manufactured fiber in which the fiber forming substance is any long chain synthetic polymer composed of at least 85% by weight of an ester of dihydric alcohol and terephthalic acid. Fabrics from polyester thread or yarn are used widely in apparel industry and homeware. The use of polyester fiber ranges from shirts and pants to jackets and hats, bed sheets, blankets, upholstered furniture and computer mouse mats. Industrial polyester fibers, yarns and ropes are essentially utilized in car tire reinforcements, fabrics for conveyor belts, safety belts, coated fabrics, and plastic reinforcements. Polyester fiber is used as cushioning and insulating materials for necessary purposes. Polyester fabrics are highly stain-resistant, have good elasticity, wrinkle resistance, shape retention, excellent wash-and-wear performance, and durability. It doesn't absorb water and can be washed quickly. Polyester fibers have good resistance to weak alkalis at high temperatures. Also, it displays a bit resistance to strong alkalis at room temperature. Weak acids have no effect on polyester fibers if it's not exposed to them for long period. Polyester fibers can show good resistance to strong acids at ambient conditions. However, if they are retained into boiling hydrochloric acid that can destroy the fibers, and 96% sulfuric acid and causes disintegration of the fibers. Polyester fibres are generally resistant to most of the organic solvents. Chemicals used in cleaning and stain removal usually aren't harmful. Polyester fiber is vulnerable to some solvents such as hot m-cresol and certain mixtures of phenol

with trichloromethane. Other solvents such as Oxidizing agents and bleachers do not damage polyester fibres. Soaps, synthetic detergents, and laundry washers do not damage it. One of the most serious drawbacks with polyester is its oleophilic attraction. It absorbs oily materials easily and holds the oil persistently.

The moisture regain of polyester is not high ranges between 0.2 to 0.8 per cent. It shows wicking, moisture can be carried on the surface of the fibres without absorption. The specific gravity 1.38 or 1.22 depending on the type of polyester fibres Polyester fibres have a density greater than other potential fibers. It doesn't possess high weight which is also advantageous for home wear activities. The melting point of polyester is ranging from 250 to 300°C. Polyester fibres shrink from flame and melt, leaving a trace of hard black residue and burns with a strong, pungent smell. Heat treatment of polyester fibres can be followed to stabilizes size and shape and enhances wrinkle resistance of the fibres. Shrinkage of the fibres also differs with the mode of treatment. If relaxation of stress and strain in the oriented fiber occurs, shrinkage decreases but the initial modulus may be also reduced. Yarns maintained at a fixed length and constant tension during heat setting are less affected with respect to changes in modulus, and reduced shrinkage values are still obtained

Chemically, polyester is primarily composed within the ester functional group. Most synthetic and some plant-based polyester fibers are made from ethylene though. They are constituent of petroleum that can also be gleaned from other sources. Most of the polyesters aren't biodegradable. Ethylene polyester (PET) is the most produced form of polyester fiber. The primary component of PET is petroleum-derived ethylene, here ethylene acts as the polymer that interacts with other chemicals to form the final fibrous compound. PET is produced by the condensation

reaction between ethylene glycol with terephthalic acid or its derivatives such as dimethyl terephthalate.

Different researches been conducted for improvement of Polyester fibers and incorporation of strong & advanced properties. C.W. Kan studied influence of high- and low-fluence laser surface morphological treatment on different polyester fibers.[16] It was found, increased wettability of polyester may be good for ordinary textile functions but bad for water resistant functional garments. It was also shown, laser irradiation could not affect the bulk properties of a polymer due to its low penetration depth, and hence, the effect of the treatment on the bulk and structural properties are limited. However, the performance and comfort properties of the irradiated polyester could be affected by laser irradiation. The laser irradiation induced ripple structures on the surface of the fibres, which eventual1y provided more air space between fibres and fabric and therefore it is possible for more air to pass through the fabric resulting in better air permeabi1ity.

Laser irradiation is claimed to largely lower the glossiness index of textile material with sharp peaks thus making the material more silk-like [17] The reduction in weight with increased laser irradiation was also observed.

In study by Keiko G. et. Al. [18], Polyester fabrics were treated by atmospheric pressure plasma (APP) to enhance hydrophilic behavior of the fiber. It was found that the APP exposure increased the wettability, oxygen concentration and roughness of the polyester fiber surface. As a result, the water wicking and antistatic property were successfully incremented. Moreover, the detergency and the dyeability were found to be improved. The study found that oily soil removal with washing and dyeability were enhanced by the plasma treatment.
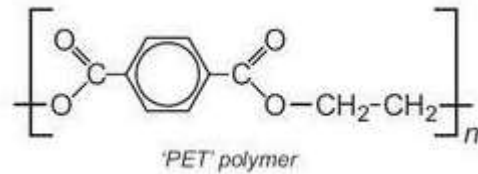
Figure 3: Chemical Structure of PET Polymer

Water, wastewater, and chemical minimization studies were carried out in a textile mill employing cotton–polyester weaving–knitting and subsequently dyeing–finishing.[19] It was found that 74 chemicals may be replaced with less toxic and more biodegradable materials. The multi-criteria decision-making methods and feasibility analysis was employed to determine potential benefits and savings for each suggested best available technique. A total of 14 best available techniques including good management practices, water minimization and chemical minimization/substitution were suggested to the mill. After the implementation of best available techniques, the following reductions can be potentially achieved; 43–51% in water consumption, 16–39% in chemical consumption, 45–52% in combined wastewater flowrate, and 26–48% in specific chemical oxygen demand load. By the implementation of 14 BATs in the mill, operational costs for water/wastewater and chemicals may be reduced 49% and 28% (annual average), respectively. The cost analysis indicated that the estimated payback periods of BATs may range from 1 to 26 months. It was found that various wastewater streams can be segregated and directly reused without treatment in the production processes. After segregation of relatively clean

wastewater streams, the remaining combined wastewater could be reused after employing advanced treatment technologies.

F. Leroux et. Al. studied the effects of atmospheric air-plasma treatments on woven and non-woven polyester (PET) textile structures. The water contact angle on plasma-treated PET decreased from 80° to 50–40°, indicating an increase in the surface energy of PET fibres due to a change in the fiber surface chemical nature. The extent of water contact angle decrease, as well as the wash fastness of the treatment varied with the structure of the textile. It was observed that the more porous the textile structure is (such as a non-woven), the fewer are the chain scissions of the PET at the fiber surface, during the plasma treatment. Thus, the level of surface oxidation and the weak boundary layers formation depend not only on plasma treatment parameters but also on the textile structure. This work demonstrated that plasma treatments not only depend on the degree of polymer crystallinity, but also on the textile structure porosity

The study conducted by Sammy Yousuf showed attempted to recovery of cotton fibers and polyester from textile waste.[20] The process was a sustainable green technology where first stage of the technology was concerned with removal of textile dyes from waste jeans using nitric acid leaching (conc. <60%) followed by the regeneration of the spent acid by activated carbon. After that, polyester was dissolved and separated from cotton by using a green switchable hydrophilicity solvent. To extract the polyester and regenerate the solvent, CO_2 was added to the solution after mixing with distilled water at 0 °C for 1 h; the solidified polyester was collected by filtration, and the form of solvent was switched back to hydrophobic through heating and corresponding CO_2 removal. Polyester was extracted from the solution by changing the hydrophilicity of solvent, thus decreasing the power consumption and polyester degradation compared with traditional solvents. According to the developed approach, the cotton fibers and polyester represented 84 and 16 wt%

of fabric, while recycling rate of the technology was >96% The results showed possibility of reaching economic returns up to 1,629 $/ton of waste and reduction of carbon footprint by −1,440 kg of CO2-eq/t of waste.

Elahe Gholamzad studied another recovery process for polyester fibers, alkali pretreatment was evaluated for improvement of ethanol production from the cellulose part of a polyester–cotton textile and recovery of the polyester[21]. The pretreatment was conducted by different alkali solutions of NaOH (12 wt%), NaOH/urea (7/12 wt%), NaOH/thiourea (9.5/4.5 wt%) and NaOH/urea/thiourea (8/8/6.4 wt%) at −20, 0, 23, and 100 °C for 1 h. All of the pretreatments resulted in improvement of enzymatic hydrolysis yield to over 88%, while it was only 46.3% for the untreated textile. The best hydrolysis results were observed by the pretreatments at the reduced temperatures (−20 and 0 °C). The maximum yield of ethanol production from the textile by simultaneous saccharification and fermentation was 70%, obtained after the pretreatment with NaOH/urea at −20 °C whereas it was only 36% for the untreated textile. The alkaline pretreatment of polyester–cotton textile at using 12% NaOH at −20 °C for 1 h is a promising process not only for improvement of the glucose and ethanol yields, but also for efficient separation of polyester from the textile with nearly its original properties. As the global consumption of fibers has increased along with the population growth and general increase of the living standards, these recovery techniques are become very important and interests of future research.

Polyamide

Polyamide is a long-chain synthetic polymer where amide linkage (–CO–NH–) links the repeating units. There are different types of polyamides from which textile fibers can be developed. Nylon is the most used term for fibers of polyamide derivatives. Nylon is the long-chain synthetic polymeric amide consisting of recurring amide groups as an part of the main polymer chain. This

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polyamide can be formed into a filament in which the structural elements are oriented in the direction of the axis [22] The first commercial polyamide fiber was nylon 6.6 and introduced by DuPont in 1938. After that nylon (especially nylon 6 and nylon 6.6) becomes one of the most important apparels and engineering materials. Nylon fibers have an attraction to different types of dyestuffs and can be dyed with direct, acid, metal complex, chrome, reactive, disperse, and pigments. Among them, only acid and disperse dyes are commercially used for their fine performance. In 2016, the global production of polyamide polymers was 7.8 million tons of which nylon 6 was 4.4 million tons and nylon 6.6 was 3.4 million tons [23] Generally, nylon fibers are represented by a numbering system. This number indicates the number of carbon atoms in its monomer molecules. Nylons made by the self-polycondensation reaction from a single monomer are presented by a single number such as nylon 6, nylon 4, nylon 7, nylon 11, nylon 12, etc. Nylons (nylon 6.6 and nylon 6.10) produced from two monomers, di-amine and di-carboxylic acids are represented by two number. The first one represents the number of carbon atoms in the diamine and the second number for di-carboxylic acids. Thus, nylon 6.10, where 6 and 10 represent the number of carbon atoms of hexamethylene diamine and sebacic acid, respectively.
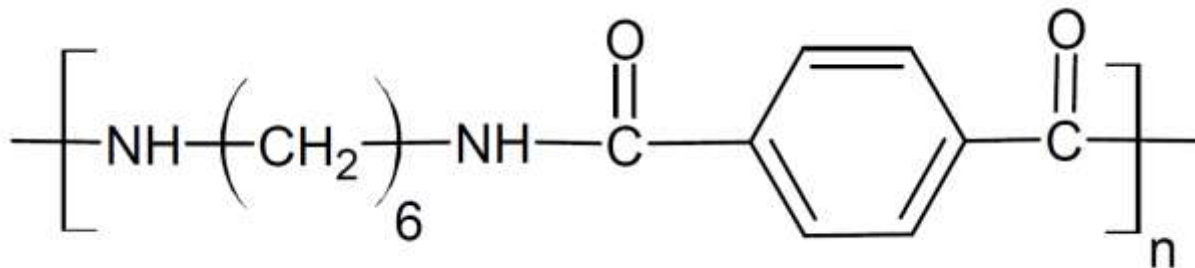
Figure 4: Chemical Structure of Polyamide

Types of Nylon Fibers:

Nylon 6: Nylon 6 polymer is produced by ring-opening polymerization (self-condensation reaction) of a single monomer named caprolactam. Caprolactam is a white crystalline compound and prepared from cyclohexanol or phenol. Polycondensation are used to polymerize caprolactam in the presence of water to open the ring structure of caprolactam. An autoclave or a reactor is used during the polymerization process. Tensile strength is of 4,200–4,620 kg/cm2 for staple fiber and 4,550–5,950 kg/cm2 for regular filament fiber, respectively. Elongation is 37–40% for staple fiber and 26–32% for regular filament fiber, respectively. Nylon fiber is elastic in nature. Regular Nylon 6.6 filament has a recovery of 100% at up to 8% extension. Nylon 6 fiber degraded by mineral acids but have good resistance to weak acids and alkalis. It dissolves in concentrated formic acid, phenol and cresol

Nylon 6.6: Nylon 6.6 fiber is produced from two monomers, one is di-amine and another one is di-carboxylic acid. Each monomer has six carbon atoms in their chemical structure and hence represents by two number, nylon 6.6. Nylon 6.6 polymer obtained by a condensation polymerization process in an autoclave. Nylon 6.6 fiber can also be produced as monofilaments, multifilament, staple, or tow form. Nylon 6.6, as well as nylon 6 fibers, are the two most used fibers in the polyamide field. Tensile strength is of 4,200–4,620 kg/cm2 for staple fiber and 4,550–5,950 kg/cm2 for regular filament fiber, respectively. Elongation is 37–40% for staple fiber and 26–32% for regular filament fiber, respectively. Nylon fiber is elastic in nature. Regular Nylon 6.6 filament has a recovery of 100% at up to 8% extension. Nylon 6.6 fiber has more resistance to acids and alkalis in comparison with nylon 6. The fiber dissolves in concentrated hydrochloric acid, sulfuric acid, and nitric acid. The fiber is insoluble in all organic solvents but dissolves in phenol and cresol.

The melting temperature of nylon 6 and nylon 6.6 fibers is (213–220) °C and (249–260) °C, respectively. The glass transition temperature of both fibers is in the range of (29–42) °C. Nylon 6 and nylon 6.6 fibers both are non-biodegradable fiber and have excellent resistance to all biological agents but both fibers are degraded by prolonged sunlight exposure with strength loss. Moisture regain of nylon 6 and nylon 6.6 are same which is 4–4.5 %.

Nylon 4: Nylon 4 is synthesized by the self-polymerization of 2-pyrrolidine. Although other polyamide fiber can be produced by melt spinning technique, nylon 4 is a dry spun fiber because it is not stable at its melting (262 °C) temperature.

Nylon 7: Nylon 7 also known as Enant fiber and developed in Russia. Nylon 7 is produced from the lactam of heptanoic acid by the condensation polymerization process. Nylon 7 is a melt-spun fiber.

Nylon 11: Nylon 11 is also a self-polymerized fiber with the commercial name Rilsan. The monomer of nylon 11 is w-amino undecanoic acid which is extracted from castor oil. The polymerization process is of the polycondensation types. Its melting temperature is 188 °C and it is a melt-spun fiber.

Nylon 6.10: Nylon 6.10 is prepared from the hexamethylene diamine and sebacic acid by the polycondensation reaction. It is also a melt-spun fiber and its melting temperature 215°C.

Nylon 12: Nylon 12 is also a melt-spun fiber like other nylon fibers and the monomer is dodecalactam which is produced from butadiene. The melting temperature of nylon 12 is 175°C.

Aliphatic polyamides are popularly used in industrial applications, such as wire and cable jacketing, cooling fans, air intake, turbo air ducts, valve and engine covers, brake and power steering reservoirs, gears for windshield wipers, and speedometers. Nylon fibers also used for power tool housings, valves, and vending for different machines and pumps and for many electrical/electronic parts including switches, sockets, plugs, and antenna mounting devices [24]. Besides the engineering and industrial applications, nylon fibers are used as essential material for making apparel items such as hosiery products, lingerie items, gloves, socks, hunting apparel, outerwear, etc. Aromatic polyamides also are known as aramids and produced by replacing aliphatic segments of aliphatic polyamides by aromatic units. In the aramid fiber, the polymer chain is highly oriented along the fiber axis and this configuration is responsible for the higher strength with a high melting point of aramid fiber. Aramid fibers are produced by the self-condensation of aromatic amino acids or by polycondensation between aromatic diacid chlorides and aromatic diamines. Nomex fiber is produced from is phthaloyl chloride and m-phenylene diamines. Kevlar fiber is produced by xerophthalmy chloride and p-phenylene diamine, they are popularly known as a high-performance fiber because of their extraordinary characteristic.

Because of it's extensive usage in apparel and textile industry, the improvement of fiber's characteristics has become a research interest. Several works attempted to enhance the properties of polyamide fibers. Maria Kanellie et. Al. attempted to remove the drawback of fiber's hydrophobicity as it is responsible for detainment of stains and static charges.[25] They followed Enzymatic surface modification of the Nylon 6,6 fabrics which is a modern and "green", eco-friendly effort. The water absorbance test reported a 2.7-fold time decrease at 10 cm for the modified sample indicating the enhancement in hydrophilicity of the final product. This enhancement was provided under mild conditions affecting only the surface of the textile material,

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delivering an eco-friendly process. Conclusively, the enzymatic surface modification of the PA fabric was effective. It leads to an increase of the polymer's hydrophilicity, while at the same time there was no impact on the mechanical and thermal properties of the bulk synthetic material.

Serge Bourbigot et. Al. studied Polyamide's flammability and investigated to create improved retardation composite system.[26] PA-6/clay nanocomposite (PA-6nano) was prepared by melt blending. Textiles have been evaluated as knitted fabrics and it is found that the heat release rate of PA-6nano evaluated with the cone calorimeter at 35 kW/m2 is reduced by 40% from PA-6. This result offers potential flame retarding textiles with a permanent effect at relatively low cost and retaining the intrinsic properties of the textile. Smoke obscuration is significantly lowered in the case of the PA-6nano fabric. PA-6nano fabric evolves smoke with a peak at 0.012 m3/s and the peak of PA-6 is at 0.018 m3/s.

The use of ultrasonic energy in dyeing PA/Lycra fabrics with reactive dyes has been studied by Nigar Merdan et. Al.[27] PA/Lycra (85/15) blends have been dyed using conventional and ultrasonic dyeing techniques with three reactive dyes. Results have shown that ultrasonic energy has affected the dye uptake and % exhaustion positively with all the dyeing. Fabric fastness properties were also measured and those results show that ultrasonic energy has not affected the light, wash and rubbing fastness. But sweat fastness of two specific dyes which are C.I. Reactive Blue 4 and C.I. Reactive Blue 15 dyes has been affected positively by the ultrasonic energy

In a study by Aysun Cireli et. Al., polyamide fabrics were changed by plasma polymerization technique utilizing acrylic acid as precursor.[28] The optimum plasma conditions for polyamide fabrics were determined as 30 W–45 min where 2 s wetting time was found. Wrinkle recovery angle of untreated polyamide fabric was 264°. In this study, after plasma polymerization of acrylic acid, wrinkle recovery angle values were increased by 13%. Any significant change

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hasn't happened in breaking strength of both fabrics after plasma treatment. In the extreme conditions of the plasma processing such as, highest applied power of 60 W at the longest exposure time, 45 min, the structure of the polyamide matrix was etched to some extend and the breaking strength were reduced to the order of approximately 1100 N which is 13% reduction in physical strength of the material. Usually this changes in the breaking strength values were less than ±1.0%. Those results showed that the mild plasma conditions were not affecting the chemical structure and physical strength of the main polymer chain.

Fernando Ribeiro Oliveira et. Al. conducted a work where three different polyamide 6.6 (PA6.6) fabrics were investigated using double barrier dielectric (DBD) plasma treatment.[29] The work showed that a relatively low DBD plasma dosage, of around 2.5 kW.Min.m-2, can effectively modify both physically and chemically the surface of polyamide fibers. The static contact angle and water drop adsorption time values were found to depend on the dosage applied: higher dosage lowers the contact angle and the time of water and dye solution adsorption. The introduction of polar groups, mainly oxygen and nitrogen from atmospheric air, is the main responsible for the improved wettability of the plasma modified polyamide fiber. The whiteness degree results obtained showed that the surface modification performed did not significantly alter the colorimetric coordinate values of the substrates. Finally, no significant modifications were obtained in the mechanical properties of the fabrics studied, confirming that plasma treatment can modify the surface properties of polyamide fiber without changing its original bulk properties. It can be considered a notable study to expand the use of the polyamide fibers in the textile industry due the improvement that can be obtained in the dyeing, printing and finishing processes after plasma treatment.

Chao Liu et. Al researched a novel aromatic polyamide (PA) reverse osmosis membrane with nanoscale water channels and hydrophilic molecular skin surface, similar to those of biomimetic neural networks, was realized for textile wastewater treatment.[30] . The cross-linked co-polymer layer of PA and DADMAC (Diallyl dimethyl ammonium chloride) was synthesized with the The polysalfone supported membrane by using a combined interfacial polymerization process and irradiation system. The water contact angle of the modified membrane was reduced drastically from 58.23° to 19.95°, and surface roughness and negative charge also decreased. Moreover, the water flux and salt rejection performances of the modified membrane improved. Water molecules, but not salts, could pass through nanoscale water channels formed by polymerization. Apart from its excellent anti-fouling property, the modified membrane was also showed robust performance for long-term separation. The integration of low-cost, high-performance, and facile strategy creates opportunity to the potential application of the proposed membrane for textile wastewater treatment. Contaminant rejection rates of modified membranes for textile wastewater treatment were investigated. The modified membrane yielded high rejection (>99%) of ion salts and high chemical oxygen demand removal (>99.3%) of organics with low molecular weights.

Polyethyelene/ Polypropylene

Polyethylene (PE) or polythene whose chemical formula $[C_2H_4]_n$ is one of the most commonly used thermoplastic polymer. A polyolefin is a polymer of olefin monomer, PE is a vinyl polymer and made from ethylene monomer by free radical chain polymerization. As of now, more than 100 million tons of PE resins are produced annually and includes for 34% of total plastic in the world[31]. PE is used in bags, toys, bottles, and thin sheets to high-performance materials such as protection vest for army personnel, sports equipment. The monomer of polyethylene is ethylene

(CH2=CH2) and ethylene is prepared either by the hydrogenation of acetylene or by the dehydration of ethanol. Ethylene also can be produced from petroleum products where this saturated hydrocarbons undergo catalytic degradation and dehydrogenation. PE can be polymerized by high-pressure high-temperature process and low-pressure low-temperature process. PE fiber is produced by melt spinning technique. The melting temp for Low Dinsity Polyethylene (LDPE) is 205 °C and 210 °C for High Density Poly-ethylene (HDPE). The molten polymer solution is extruded into a spinneret as fine jets of fiber and when it is cooled to normal temperature we get desired fiber filaments. After that, the monofilaments might passed a series of drawing roller and the draw ratio depends on the application of PE. In case of HDPE, the drawing process is carried out at high temperature to ensure more crystallization of PE, first the monofilaments are heated by hot water at 100–125 °C and then passed over 115– 120 °C heated rollers[32]

All types of PE have excellent resistance to all types of acids and alkalis for which it is desirable in different industry. Exceptions are hot concentrated sulfuric acid and nitric acid which gradually dissolve the LDPE and MDPE[33]. PE also has good resistance to bleaching agents and organic solvents as well. PE fibers have excellent protection from insects, bacteria, fungus, mildew, and other microorganisms There are some materials though which can create the damage gradually, such as PE swells and may ultimately dissolve in chlorinated hydrocarbons and aromatic solvents such as benzene, toluene, and xylene. Low melting point can be counted as disadvantage of PE in many high-performance applications, the softening temperature for LDPE and MDPE is 85–96 °C. Brittleness temperature of PE is less than −114 °C, which indicates that PE can retain

its flexibility for long range of temperature. Burning of PE is slow and melts before to propagating flame so as a material it's fire safety factor is better than other polyemers.

Polypropylene (PP) with the chemical formula $(CH_2=CHCH_3)n$ is another member of the polyolefin group's which is one of lightest member produced from propylene monomer. The global demand for PP polymer was about 60 million tons in 2015 and it is expected that it will hit 120 million tons by 2030 [34]. Methyl group of the repeating unit of PP which replaces one of the hydrogen atoms of PE's repeating unit. The propylene monomer is flammable nontoxic gas. Polypropylene polymer is produced from propylene gas in the presence of catalysts such as Al (iso C_4H_9)3 and $TiCl_3$ or Al $(C_2H_5)_3$ and $TiCl_3$ with an addition polymerization reaction carried out under 10-atmosphere pressure and below 80 °C. Melting temperature of PP polymer is 163–171 °C, therefore, the melt spinning process is suitable to produce fiber from PP [34]. The melted polymer is extruded through a spinneret to form the fine filaments, the fine jets are subject to a drawing process at high temperature to orient fiber axis. Similar to PE, PP fiber has excellent resistance to acids, alkalis, bleaches, and most solvents but nitric acid can deteriorate the fiber at a high temperature. Other elements where PP is vulnerable are xylene, perchloroethylene, and 1,1,2,2 tetrachloroethane. The melting temperature of PP fiber is 163–171 °C, the fiber softens at 150– 160 °C, and decomposes at 290 °C. PP fiber does not absorb moisture which makes it hydrophobic in nature and nonbiodegradable. PP fiber also shows good resistance against bacteria, mildew, insects, fungi, i.e., the fiber cannot digest by these biological agents. PP polymer is used to build package films, pipes, storage tanks, seat covers, bottles, toys, filters, ropes, tapes, twine, and in the automobile industry, apparel textiles, home textiles, and non-woven products. In medical science, PP materials can be vitas as they are used to make non-absorbent suture and transvaginal mesh are produced.

Researched has been conducted in recent years with these two polymers to enhance and attribute properties. Ali Rizvi et. Al. studied modification of the mechanical and rheological properties of polypropylene (PP) is done through the in-situ creation of polyethylene terephthalate (PET) fibrils.[35] The technique enhances the tensile strength which is governed by draw ratio of PP fibers by up to 46% and elongation at break by up to seven-folds. Strain-hardening behavior in the fiber-spun PP/PET was observed, which is not observed in the neat PP or in the melt-blended PP/PET. When the PET domains are fibrillated, the storage (G′) and loss (G″) moduli increases indicating that the fibril network responds elastically over long timescales. The presence of γ-polymorph crystals of PP in was present both PP and the fiber-spun PP/PET. Foam extrusion is used as a model polymer process to study the effect of the PET fibrils on the processability of PP. The research found the presence of PET fibrils in PP yields foams that exhibit up to two orders of magnitude higher cell densities.

C Zhang showed improved properties by blending Vapor Grown Carbon Fiber (VGCF) into PE and PP fibers.[36] The improvement of electrical conductivity was observed and the reason for that was the selective location of VGCF in the HDPE phase. A double percolation is the rudimentary requirement for the conductivity of the composites where first one is the percolation of carbon fibers in the HDPE phase and the other one is the continuity of this phase in the polymer blends. The percolation threshold of short carbon fiber filled HDPE/isoPP (50/50) blends, 1.25 parts per hundred parts resin VGCF content, is lower than those of the individual polymers. It can be seen that carbon fibers are preferentially positioned in the HDPE phase.

Zijian Dai et. Al. utilized PP and PE fiber for air purification system with addition of anchored nanocrystalline MnO2.[37] The research constructed a multifunctional composite filter combined with nanocrystalline MnO2 and PE/PP bicomponent fibers. A novel redox process was

used to synthesize α-MnO2 and δ-MnO2 with outstanding catalytic capacity for HCHO. The δ-MnO2 synthesized via the redox method was found to have the highest content of manganese vacancies, species and mobility of adsorbed oxygen. The δ-MnO2 exhibited the best HCHO oxidation performance at low temperatures and was further chosen to fabricate an MnO2/PE/PP carded filter with filtration, adsorption and catalytic abilities. A composite PE/PP nonwoven mat with uniform dispersion and anchoring of MnO2 was structured in this work. An as-prepared MnO2/PE/PP exhibited excellent catalytic activity for HCHO. Moreover, after a MnO2/PE/PP sample exhibited a relatively high filtration efficiency of 71.73%, a low pressure drop of 6.02 Pa and an improved quality factor of 0.2219 Pa−1. The manufacture of this MnO2/PE/PP filter was very easy to build.

Others

Polytetrafluoroethylene (PTFE) is a thermoplastic, vinyl group polymer with $(C_2F_4)n$ as a chemical formula PTFE differs from major vinyl group polymer is that in polytetrafluoroethylene four hydrogen atoms of the vinyl group have been substituted by fluorine atoms. Teflon is the most common brand name of PTFE. PTFE produced by fluorination of chloroform by hydrogen fluoride in a two-step process yielding CHCIF2[38]. PTFE is a highly crystalline polymer and its melting point is also high around 330 °C and the polymer begins to decompose before melting. PTFE polymer is not soluble in commercial solvents. So, melt spinning, dry spinning, and wet spinning are not very effective technique for this polymer. There is one special spinning mechanism, which is used for the infusible and insoluble polymers is used to produce textile fiber from PTFE polymer. PTFE fibers have extraordinary resistance to all types of acids, alkalis and most solvents a few perfluorinated organic liquids can dissolve PTFE at very high temperature around 300C.

PTFE fiber has the best thermal stability among all known synthetic fibers. The melting point of PTFE fiber is around 330 °C. The application temperature range of the PTFE polymer is −73C to 275C. PTFE fiber is fully hydrophobic in nature and does not absorb any moisture and non-biodegradable fiber. The PTFE fiber is not influenced by any types of insects and microorganisms and inert gas in sunlight. The PTFE is inert polymer in all conditions and medium which makes it an outstanding material numerous high-tech and industrial applications. PTFE used in the coating in non-stick frying pans and other cookware, braided packing, filtration fabrics, gaskets, laundry pads, conveyor belt, electrical tapes, corrosion resistance cordage, electrical insulator, and water-repellent composites. Teflon fibers are also used in the aerospace and aviation industry as well.

Polyvinyl chloride (PVC) with the chemical formula ($-CH_2-CHCl-$)n, is a polymer polymerized from vinyl chloride, a widely used plastics and rigid, inert and non-toxic polymer. In commercial trade, the PVC is known as vinyl resins.[39]The production of the vinyl resin increases year by year and used in a versatile range of products such as siding, windows, wiring, cables, pipes, household products and a much smaller scale in textile fiber. In the industrial production process most of the polyvinyl chloride is formed by the suspension polymerization process. Emulsion and bulk polymerization process are also utilized on a smaller scale to produce PVC polymer. The spinning of PVC fibers can be carried out by melt or dry spinning process. Melting temperature of PVC polymer is (120–130) °C and begins to decompose at about 200 °C. So, the spinning temperature should be kept below 200 °C.[39] Very fine filament fiber can't be produced from this method, dry spinning method is more suitable for this purpose. PVC fiber can be categorized into these fibers: Polyvinyl chloride fiber (contains 100% vinyl chloride units); Vinyl chloride copolymer fiber (contains at least 85% vinyl chloride); chemically modified polyvinyl chloride (contains less than 20% vinyl chloride and more than 80% vinylidene chloride units).

PVC polymer and fiber have strong resistance to all acids, alkalis, bleaching agents, reducing agents, and oxidizing agents. It's also doesn't affect by alcohols, ether, and petroleum hydrocarbon however the PVC fiber will swell and ruin it's structure by phenols, toluene, trichloroethylene, benzene, and acetone. Melting temperature of PVC polymer is 120–130°C and decomposition temperature at about 200 °C. PVC fibers are non-biodegradable and isn't vulnerable to insects and microorganisms. The fiber does not swell in water because it has no water absorption. PVC polymer is used in windows, water pipes, wadding's, filter cloths, braiding, battery fabrics, awnings, curtains, artificial limbs, billiard clothes, accessories for different machinery, and so many other things.

Polyacrylonitrile (PAN) is also a vinyl group polymer with the chemical formula of (–CH2–CHCN–)n. PAN polymer is produced from acrylonitrile monomer. Acrylonitrile mainly produced from acetylene. Hydrogen cyanide and acetylene are used in reactions to produce acrylonitrile at (80–90)°C in the presence of ammonium chloride as a catalyst. The PAN fiber can be produced different spinning processes such as melt spinning, dry spinning, and wet spinning technique. But commercially melt spinning process is not viable as the stable phase of molten PAN polymer isn't obtainable. In the dry spinning process, dimethylformamide is used as only solvent, and in wet spinning process many solvents can be used such as dimethylacetamide, dimethyl sulfoxide, nitric acid, and zinc chloride .It has a tensile strength of 2,100–3,150 kg/cm2 for staple fiber and 3,500– 5,250 kg/cm2 for filament fiber, respectively. It can be elongated to 20–55% for staple fiber and 30–36% for filament fiber, respectively. The elastic recovery of PAN fiber is 90–95%. Acrylic fibers have excellent resistance to acids, alkalis, oxidizing agents, and reducing agents. Only strong acids can create damage on PAN fiber and it can be slowly hydrolyzed by weak bases. Acrylic fiber is a non-biodegradable fiber and is not attacked by microorganisms and

insects. The PAN fibers have a high melting point, (330–340)°C and it starts to decompose before melting temperature. Acrylic fibers have a varied range of industrial applications. It is used to produce knitted outerwear, carpets, furnishing fabrics, outdoor fabrics, flocking for flock print, tufting, paper, core-spun yarns, etc.
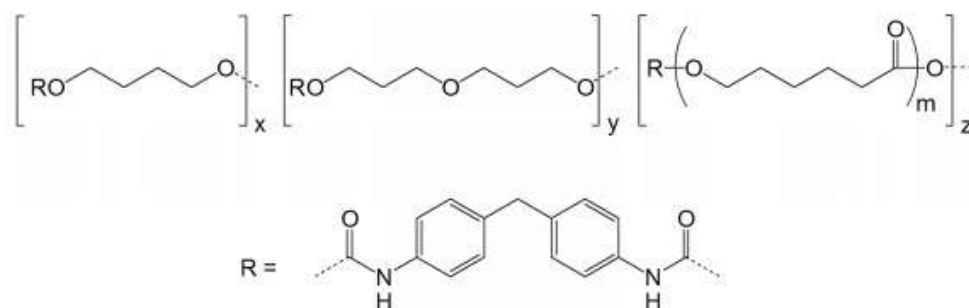

Fig 5: Chemical Structure of Polyester-Polyether Polyurethane

Polyurethane

Structure

Polyurethane (PU) is a polymer made of organic parts connected through urethane links. It can be both thermoplastic or thermoset materials though most of them are thermoset. PU chemical structure is a multiblock copolymer comprising alternating soft polyester or polyether

and hard polyurethane–urea segments. These are the two main phases of Pu structure which can be differentiated by hard and soft segments. Their hard and soft segments are ensured by keeping them respectively below and above their glass transition temperature. This is the reason for PU being used in versatile applications because the long structure can be alternated, and different physical properties can be incorporated. The structure can be shuffled by changing the length or molecular weight of each segment. The soft segments are dihydroxy terminated long chain polyols with low molecular weight (Mw = 500–5000 g/mol) such as polyethers, polyesters, polydienes and polyolefins. Hard segment produced by the reaction of diol/diamine/diisocyanite This Rigid segment holds difunctional l(each has two group) isocyanaite which can be aliphatic or aromatic according to intended property inclusion. Basically, long flexible chain mostly provided through

polyols give soft, stretchy or elastic polymer whereas short chains with high no. of crosslinking gives hard polymer[40].

Properties

The properties of PU greatly is related to it's structure. One of this polymer's great advantage is tailoring the properties to have high strength, high rigidity or high flexibility and toughness. They usually have good resistance to oil, hydrocarbons, oxygen, and ozone. However, PU are vulnerable to microbial attack and UV light, the later can discolor the material.

The three most important commercial aromatic isocyanates are toluenediisocyanate (TDI), diphenylmethane diisocyanate (MDI), and naphthalene diisocyanate (NDI) . Toluene diisocyanate is available as a mixture of two isomers: 2,4-TDI and 2,6-TDI . MDI and TDI are two materials to produce thermoplastic elastomers and foams, while the polymeric version of MDI and TDI are often specifically chosen for coatings, sealants and adhesives. Aliphatic isocyanates have huge

importance and used as hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) and hydrogenated MDI (HMDI). PU made with these isocyantes don't lose their color under the exposure of UV light and are less susceptible to oxidation and degradation. Only problem is they are more expensive. For this reason, aromatic isocyantes have eclectic range of application. They are chosen when UV light exposure can't be a huge problem whereas aliphatic isocyantes are preferred for more applications. An important triisocyanate is triphenylmethane triisocyanate which has applications in the coating and adhesive industries.

Polyurethanes obtained from aromatic isocyantes and low molecular weight diols have high glass transition temperatures and it makes them very brittle, whereas PU obtained from aliphatic isocyantes and polymeric diols have much lower glass transition temperatures (Tg's) The majority of commercial PU are available as form of elastomers. They can be made by vulcanizing to avoid crosslinking the polymer chains. The highly elastic network combined with alternating flexible polyether/polyester blocks and rather short and hard urethane blocks. The urethane blocks are found in hard domains that are connected via hydrogen bonds. These domains are physical crosslinks and provide a storing force when the thermoplastic urethane elastomer is stretched.

Most elastomeric polyurethanes are polyester/polyether based. The soft segments takes the larger portion of the elastomer and determine the physical properties of the elastomer. Polyester-based urethane elastomers have better oxidative and high temperature withstanding than polyether-based polyurethanes, In terms of , hydrolytic stability and low-temperature flexibility, polyester based PU aren't better versions.Commercially, polyethers are usually more expensive than polyesters.

The cheapest polyether polyol can be found is hydroxyl-terminated polypropylene oxide (PPO), also called polypropylene glycol (PPG). Another important polyether polyol is based on polytetramethylene oxide (PTMO). Both of them have low melting temperatures and very low Tg's (190 - 200 K).1 Polyurethanes based on PTHF typically shows higher stability than PPG based urethanes, due to PTHF's ability to crystallize under stress. Polyol for the manufacture of elastic urethane fibers are commercially practiced such as Spandex (Elastan) for stretchable fabrics.

Polyester polyols are mostly made from adipic acid and ethylene glycols (polyethylene adipate), or from butanediols and adipic acid (polybutylene adipate). Both of them are crystalline above room temperature. To reduce crystallinity, copolyesters are often prepared from a mixture of glycols and adipic acid. Another important polyol is polycaprolactone diol which is biodegradable polyester with a low melting point of about 330 K and a glass transition temperature of about 210 K. It is sometimes copolymerized to reduce the crystallinity. This diol is mostly used for the manufacture of commercially specialized polyurethanes.

Application

Among different applications of PU, one of it's notable utilization is textile industry including sportswear, weather resistant workwear and medical textiles. These industries require breathable and waterproof cloths to ensure optimize level of comfort and highest level of safety. Millions of garments are producing PU-PEO films as a barrier on their cloths to create balanced level of breathability, waterproofness, durability [41]. The waterproofness and water vapor movement is ensured in two different structures-hydrophilic and microphase membrane. Microporous structure have a degree of breathability through it's pore and waterproofness is ensured via the pore size. Hydrophilic structure acts as solid without any gap so it has good waterproofness and air particles or moisture movement from both side is ensured by an absorption–

diffusion–desorption mechanism. PU is a well known polymer for it's capability to control moisture. PU used as Shaped Memory Polymer(SMP) can control it's moisture accessibility through the change in it's chain flexibility or molecular weight of polyol, structure of hard segment and the type of chain extender that is used. Through these parameters, Glass Transition Temperature (T_g) can be changed and discernable difference in moisture permeability is seen at above or below the T_g. Heating PU above the T_g increases the soft segment into a larger volume on the micro-Brownian movement, which leads to expansion of non-physical void and high transmission of water molecules .As a protective wear, PU coating with specific nano additives is proved to be usable as fire retardant . PU/clay nanocomposite or PU/ polyhedral oligomeric silsequioxanes (POSS) appreciably attenuates the ramification of fire propagataion[42]. PU coating with these additive shown generally reduce total heat release, the diffusion rate of flame, the production of smoke and its toxicity.

Polyurethane (PU) has also been widely used in biomedical applications due to its biocompatibility and mechanical properties. Artificial blood vessels can meet their biological requirements with supramolecular structures. It is molecular complexes in which biological polymers are formed by specific intermolecular interactions with specific molecule. The vessels must have sufficient mechanical strength to withstand blood pressure. PU/PCL (Polycaprolactone) hybrid scaffold shows great potential to be utilized as blood vessel.[43] The scaffold made of PU composite shows greater and improved tensile strength. The blend scaffolds induced no cytotoxicity, showing no evidence of causing cell lysis or toxicity. Artificial blood vessels needed to be porous to provide nutrients and oxygen in purpose of healing process. The pores have to be within range of 5 to 150 μm. If it is less than 5 μm, the growth of granulation tissues out of a living body blood vessel at an anatomized portion cannot be suppressed and when it gets bigger than 150

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μm, unevenness on the inner surface of artificial blood vessel gets increased leading to thrombus formation. PU/PCL composites with PU nanofiber can be used for preparing tubular scaffolds with high porosity. This composite also shown better results with endothelial cell growth and anti-platelet adhesion of the artificial blood vessels. PU fibers can reinforce a hydrogel structure when deposited onto the surface. This sort of soft tissue structure can be utilized as cartilage or vertebral disc.[44] This fibrous matrix on Epoxy-amine based hydrogel assembly have increased it's mechanical strength, toughness and harness of swellability. It is found that, five percent fiber reinforcement (w/w) improves the tensile modulus of hydrogel from 0.7MPa to 2.5MPa, breaking strength from 0.2MPa to 1.3MPa and breaking strain from 30% to around 150%.[45]

PU has shown great potential to act as filter medium with high filtration performance. Polyurethane filters with mean fiber diameters in the range of 150–250 nm were prepared by electrospinning and use it as filter media.[46] The fiber diameter found controllable with solution concentration, electric field and tip to collector distance. The PU nanofiber filtration media has shown potential to collect particle in the range of 80–100 nm. Specially prepared PU fibers mats can be developed with high sorption capacities for volatile organic compounds(VOC).[47] Compared with activated carbon as absorbent, PU fiber showed efficiency in regards of recovery treatment. Fibrous mat of PU can be reused by disruptions under ambient conditions. This filter has the advantage of avoiding harsh thermal treatments for regeneration needed to remove the chemisorbed monolayer on the exposed surfaces like the one happened for activated carbon. When fibrous PU mat filter is tested with hexen, toluene and chloroform, it is found that polar nature of the aromatic and chlorinated VOC compounds and their ability to interact with the building blocks of the polyurethane determine the filtration performance. So, it is recommended to alter the rigid

and soft diol constituents of the PU polymer to change the blocks to interact effectively with particular type of VOC. Similar work where PU is loaded with thermal powerplant byproduct fly ash particles(FAPs) works as an economically and environmentally-friendly nonwoven matrix for outdoor and indoor VOC filtratio[48].Incorporation of FAPs in PU solution increased solution conductivity and viscosity, resulting in smaller nanofiber diameters for composite fiber .FAPs are well dispersible in PU and capable of increasing mechanical strength up to certain percentage. The absorption capacity of PU fibers improved with increasing amounts of FAPs, PU fibers with 30 wt% FA showed the highest VOC absorption capacity, which was 2.52–2.79 times (for five VOCs) greater than that of pristine PU fibers. It's unchanged efficiency of VOC absorption during cyclic use demonstrated the completely reversible absorption and desorption characteristics. Tortuously structured PVC/PU fibrous medium with is found robust mechanical and filtration performances via electrospinning.[49] PVC/PU membranes as core filter medium were deposited on the filter paper. The resultant membranes exhibited relatively high tensile strength (9.9 MPa), good air permeability (154.1 mm/s) and excellent abrasion resistance (134 cycles), which also showed fascinating filtration performances toward NaCl aerosol particles in terms of a high filtration efficiency (99.5%), relatively low pressure drop (144 Pa), and more lightweight (less than 21 g/m2). PC(Polycarbonate)/TPU blend membranes with added PVP-poly(vinylpyrrolidone) were prepared via non-solvent induced phase separation(NIPS) by blending TPU in purpose of improved wastewater treatment.[50] TPU played the role of pore formation agent in the membrane and increase the sponge like structure in the blend. More TPU dosage was increased in casting dope, the mean pore size and pure water flux of blend membranes raised. The blend structure shows an increment in pure water flux, membrane hydrophilicity, flux

recovery ratio and membrane porosity. The discussed structure also inherited better average roughness that leads to reduced amount of fouling.

PU nanofiber has shown tremendous prospective in wound healing and biomedical application by developing antibacterial membrane because of it's oxygen permeability and excellent barrier properties. PU is resistant to microorganisms and abrasion with high hydrolytic stability. To achieve antibacterial activities, PU fibrous membranes was made by electrospinning the polymer followed by plasma pretreatment, UV-induced graft copolymerization , quaternization reaction and addition of poly(4-vinyl-N-hexyl pyridinium bromide) on the surfaces.[50] Antibacterial assays showed that the modified PU fibrous membranes possessed highly effective antibacterial activities against both Gram-positive S. aureus and Gram-negative E. coli. Tourmaline (TM) nanoparticle (NP)-decorated PU composite nanofibrous mats is synthesized with antibacterial and superhydrophilic functionalities.[51] TM NPs in PU solution increased the solution conductivity and viscosity, resulting to thinner nanofiber. PU is hydrophobic in nature but with TM nanoparticles the hybrid turns into superhydrophillic nature. Besides the composite turns more robust with 75% increase in tensile strength. However, the overarching trait of the fibrous membrane was it's outstanding antibacterial activity showed by strong protection against E. coli and Enterococci bacteria. Ciprofloxacin HCl (CipHCl), a fluoroquinolone antibiotic, is one of the most widely used antibiotics in wound healing. A composite nanofibrous wound dressing material of PU–dextran loaded with CipHCl was obtained through electrospinning to perform tissue regeneration and antibacterial activity[51]. It showed expected performance against gram positive and negative bacteria. Propolis loaded PU composite nanofibrous scaffold can successfully be fabricated using electrospinning process. The combined structure shows improved physiochemical

and biological characteristics. The composite shows good antibacterial activity against gram negative bacteria (Escherichia coli) along with enhanced cell viability in the cytocompatibility test.

PU is reported to combine well with both multi and single wall carbon nanotube (MWCNT/ SWCNT). Presence of MWCNT can facilitate a web like structure among collected fibers of fine diameters around 350nm. Individual and aligned fibers grow outside surface of fibers to form web shape. PU/MWCNT composite mat is found with better mechanical and structural characteristics. The composite mat is highly porous and had a density equivalent to about 1/4–1/3 of the bulk density of PU.[52] With proper functionalization and homogeneous dispersion of MWCNT in Pu fibers can provide with higher modulus, elongation at break and better surface roughness. Single-walled carbon nanotube (SWNT) can reinforce PU as well, tensile strength of ester treated SWNT-PU membranes is enhanced by 104% as compared to electrospun pure polyurethane membranes, while an increase of 46% was found in only SWNT dispersed polyurethane matrix. Tangent moduli shows an increase of 250% and 215% respectively in the mentioned cases.[53]

Fiber Processing

Polymer needs to be converted to a liquid or semiliquid state, either by being dissolved in a solvent or by being heated until molten to process it further as fiber. The liquification frees the long molecules from attachment with one another, allowing them to move freely. The processed liquid is extruded through orifice in a device known as a spinneret, forced out as fine jets of liquid that harden to form solid structure with all the resemblance of a very long fiber or filament. This extrusion of liquid fibre-forming polymer, is known as spinning. Several spinning techniques are used in the production of man-made fiber, including solution spinning melt spinning, gel spinning and emulsion spinning, electrospinning and forcespinning.

One of the most utilized methods for the preparation of man-made fibres is solution spinning introduced industrially at the end of the 19th century. Solution spinning includes can be classified as wet and dry spinning. The former method was initially used to produce rayon fibres, commercially and the latter method was used to spin cellulose triacetate to acetate fibres. In both methods, a viscous solution of polymer is passed through the tiny holes of a spinnerets.

During wet spinning the spinnerets is generally placed in the spin bath, in which solvent spreads out of the extruded material and a nonsolvent diffuses into the extrudate. The resulting product may be oriented by stretching during this stage, or the freshly formed fibres may be stretched after they are removed from the spin bath. At this form containing solvent and nonsolvent, is washed with more nonsolvent. A lubricant used as the fibre finish, is generally applied before the fibre is heated to dry. The fibre is then wound onto spindles or sent to a cutter to process in final shape.

The most economical method of spinning is melt spinning because there is no solvent to be recovered and the spinning rates are greater than most other methdos. In melt spinning, a viscous melt of polymer is extruded through a spinneret containing many holes into a process zone called the spinning tower. There the molten polymer is solidified by a huge amount of speedy cold air, and then fibers are collected as well as processed further according to application. In a process known as spin-drawing, fibres may be drawn in-line to several times upto their original length. Then the fibers may be collected directly from the spinning tower which is considered as continuous filament. Melt-spun can be useful to produce a monofilament at which a single-hole spinnerette is used to yield that is of much larger diameter than usual textile fibres. Drawing may be done in-line or as a part of a different step.

Gel spinning is another used technique that has come into use commercially around 40 years ago. As originally applied, solutions of very high solid contents were used; such solutions were similar to semisolids as 20-80% of the solution can be solid. This process had been improvised since then, polymer of an extremely high molecular weight is dissolved in a solvent of low concentration making a very viscous solution. This solution is still retaining significant amount of the solvent, is actually a gel of polymer and solvent. In this state, the fibre can be stretched in order to pull the molecules of the polymer into an elongated state. Very high strength and high-stiffness polyethylene fibres are commercially produced using gel-spinning techniques.

For some nonmelting and insoluble polymers can be processed to a finely grounded powder, mixed into a solution of another polymer, and solution-spun to fibres. The soluble polymer can be exasperated by a solvent or this can be done by burning and the residual fibre collected. For polymers with high melting points, this process can be used to make fibres of fluorocarbons. Even materials that are not polymer such as ceramics can be suspended in a solution of a cheap polymer such as cellulose and spun to fibre. The cellulose can be burned away to leave a lumped mass in fibre form which can be used. Such fibres are used as replacements for hazardous asbestos fibres.

Electrospinning process is comparatively complex process and is associated with the interaction of several physical processes that are separately instable. The processed electrospinning jet is composed of four parts: the base, the jet, the splay, and the collection. In the base region, the jet emits from the needle to form a cone known as the Taylor cone. The shape of the base is dependent combination of the surface tension of the liquid and the force of the electric field. If the electric field is strong enough to pull the jets then it can be ejected from surfaces that are essentially flat. Solutions of higher conductivity are easy for jet formation.Then

the electric forces accelerate and stretch the polymer jet, causing the diameter to decrease as its length increases to produce fibers. If solvents have high vapor pressure then it may begin to evaporate, causing a decrease in jet diameter and velocity producing less fibers. The charge repulsions cause the jet to split into many small fibers of approximately equal diameter and charge per unit length[54] . Rutledge et al. have reported high speed images with times as low as 18 ns to demonstrate that the jet that appears to splay is actually a single, rapidly whipping jet. After traveling to a short distance in high electric fields, the jet becomes unstable, begins to whip with a high frequency, and undergoes bending and stretching [55]. Rutledge et al. studied the competition between these instabilities for various applied electric fields, flow rates, and determined the dominant mode.

The electrospinning process is highly adaptable. It allows not only the processing of many different polymers into polymeric nanofibers but also the co-processing of different polymer mixtures. This is workable for mainly research activities as it can be used ever for mixtures of polymers and low molecular weight non-volatile materials. Different structures like polymer blend and core-shell and side-by-side bicomponent electrospinning have growing research areas that are connected with the electrospinning of multicomponent systems. In the process it is possible to create nano-fibers of an 'unspinnable' material or to adjust the fiber morphology and characteristics. The technique also provides the capacity to lace together a variety of types of nanoarchitectures to be encapsulated into an electrospun nanofiber.

The electrospinning process is characterized by a quick evaporation of the solvent in solution spinning. Although structure formation happens at a millisecond scale, the degree of crystallinity and the perfection of the crystals which grow within the fibers are like those observed for thicker fibers as obtained. Another feature is the strong deformation taking place

during the whipping mode, which tends to give rise to orientational processes High degrees of crystal orientation have been observed for various electrospun polymers.[56]

Among all the processes, Forcespinning™ is comparatively new and has been developed to make nanofibers from a wide range of materials. This new method uses centrifugal force, rather than electrostatic force as in the electrospinning process.[57] The Forcespinning™ method uses either solutions or can be applied on solid materials that are solution or melt spun into nanofibers. The morphology of the nanofibers can be varied with control of rotational speed of the spinneret, collection system and temperature. Orifices of the spinneret can have modified and controlled geometric shapes to provide desired cross-section of nanofibers. The Forcespinning™ method has been successfully used to make nanofibers of poly-ethylene oxide, poly-lactic acid, bismuth, polypropylene, acrylonitrile-butadiene-styrene, polyvinyl pyrrolidone, and polystyrene among others.[58]

The Forcespinning technique has several features one of them is tunable fiber deposition to ensure accurate cross directional coating uniformity, and also adaptable to substrate web widths.[58]The Forcespinning system has the capability for dual materials feed thus allowing the continuous materials feed system especially for melt and solution spinning with no material dielectric requirements. Additionally, the FS system has an almost 100% yield and solvent-free processing for melt spinning with melt temperatures up to 350 °C. This thus eliminates the direct operating expense and environmental burdens. The method is capable of producing nanofiber from either solutions or pure molten materials. This FS technology requires less solvent or no solvent at all (i.e. melt Forcespinning), thereby making it a more cost effective method with better safety of operation compared to electrospinning

Forcespinning VS Electrospinning

As of it's growing interest, mass scale production of polymer nanofiber is a challenge for researchers. Electrospinning had been mostly used for this purpose because of it's potential industrial level of production. This method was developed by Morton and Coley in 1902. Doshi and Reneker developed the method and reintroduced it to create fibers. [57] But for it's certain number of limitations other methods stands a chance to be it's good alternative. The electrospinning process consists of driving a polymer solution jet through a high electric field. This electric field is mostly higher than 10KV which made the process associated with high electrostatic force leading to high power consumption. The number of solvents used in the methods are limited because of maintaining certain level of vapor pressure, viscosity and surface tension. The solvent needs to remain in specific range of dielectric constant to operate. Mostly, the fiber yield from electrospinning process is not very high. To overcome these limitations, a comparatively novel and feasible method named Forcespinning is becoming popular. Forcespinning method use centrifugal force to spin the loaded solution or melt to produce fibers. A spinneret is designed to assist in this purpose to draw nano level fibers from it's orifice. Expelled fibers are collected from collectors which are placed circularly surrounding the spinneret. Drawing fine fibers from the solution of polymers is dependent on spinneret angular velocity and orifice radius, polymer viscoelasticity (which includes viscosity and relaxation time of the material), surface tension, evaporation rate (for solvent in solution) and temperature (melting and solidification), and distance of spinneret orifice to collector. [58]Centrifugal force applied on the jet enables the solution to overcome its surface tension to produce fibers. Forcespinning method replaces the electrical force with the rotational force and incorporate easier yield.[59] Forcespinning method removes the constrains of nonconductive solvent. The

centrifugal force helps fibers to elongate while in electrospinning the fibers get to stretch because of electrostatic force which needs the solvent being necessarily a conductive one. Moreover the Forcespinning method gives the flexibility to use melt solution of solid materials as well. As melt can be directly produced from materials without any help of chemical compounds, the method is free from cost involved in the chemical recovery steps. Heated solution is also affordable in the technique by heating the spinneret in purpose of holding it. Another disadvantage of the electrospinning method is low production rate of fibers. At lab scale production, apparatus and the system produce fibers at .1gm/h rate whereas for Forcespinning method it is around 1gm/min. The fiber yield rate is significantly higher for Forcespinning and so does the ease of production. Forcespinning facilitates production of nano range fibers with the help of specially designed spinneret and its orifice. Developed system which includes high rotational speed and good thermal stability is also the reason of small diameter fibers

Fiber Characterization

Once nanofibers or films have been produced they needs to be characterized to determine the their properties and the process to enhance them. DSC, TGA are very popular characterization methods have been used to determine the thermal stability of the fibers, with parameters such as thermal degradation, melting temperature, transition temperature, crystallization temperature, and degree of crystallinity present. Another important characterization method is X-Ray diffraction to determine the atomic structure and configuration of the nanofibers. Infrared Spectroscopy is vital for determining chemical contents of the samples; it determines functional groups and its configuration and concentration within the sample. This test helps to find out evaporated or left traces behind, and whether depending on the configuration of the functional groups, the material created will have the desired properties. One

of the most basic characterization methods relies on statistical analysis for fiber diameter; using SEM pictures of the tested sample, with a measurement program, the diameter of the fibers can be measured, and average diameter calculated. Minitab, OriginPro, Excel different software are used for these purposes. using the SEM, the morphology of the fibers can be analyzed, whether it is a rough or a smooth texture; whether the fiber is attached with each other ,whether they contain beads or whether there is a certain degree of alignment in the sample. The scanning electron microscopy (SEM) images demonstrated that the point-bonded structures of fiber mats played an important role in the load-bearing component as determined in loading-unloading component tests, which can be considered to have a force of restitution.[60]. Demir et. Al, Studied SEM images of the obtained from electrospinning of PU/DMF solutions with four different concentrations, which are: (a) 3.8, (b) 5.2, (c) 10.1, and (d) 12.8 wt%. [61] An increase in solution concentration results in fibers with larger diameters. The dependence of the average fiber diameter (AFD) on solution concentration is shown. X-ray diffraction (XRD) analysis is a useful tool for obtaining information about crystalline structure of semicrystalline polymers with a range of inter-atomic distances from 0.1 to 5 nm[62]. Glass transition and melting temperatures of the different segments of polyurethane fiber mats can be obtained using differential scanning calorimetry or DSC. Dynamic mechanical analysis (abbreviated DMA) is another technique used to study and characterize Polymer fibers. It is most useful for studying the viscoelastic and mechanical behavior of polymer fibers. A sinusoidal stress is acted in the device and the strain in the material is measured, allowing one to determine the complex modulus. The temperature of the sample or the frequency of the stress are altered to vary in the complex modulus. In this way, glass transition temperature of the material, as well as to identify transitions corresponding to other molecular motions can be figured out. Thermogravimetric Analysis which measures mass

loss as a function of temperature is also commonly used to fully characterize polymer fiber. The number of steps present in a TGA graph correspond to compounds that consists the material. One step corresponds to a homogenous material while many steps relates to material made of many different compounds such as alloys or composites. A shift in thermal degradation correlates to a change in the thermal stability of the material as reported by Achaby et. Al.[63]

Smart Textile

The term 'smart textiles' is related to intelligent or smart materials; it was first conceived from Japan. The first textile material can be considered as a 'smart textile' was silk thread having a shape memory effect which is generally accepted as the birth of real smart materials. It was around 1990s that intelligent materials were associated in textiles. Smart textiles definition can be constructed as textiles that are able *to sense* stimuli from the environment, *to react* to them and *adapt* to them by integration of functionalities in the textile structure. The stimulus as well as the response can have an electrical, thermal, chemical, magnetic, or other origin, the extent of intelligence can be divided in three subgroups [64]. They are: 1. passive smart textiles can only sense the environment, they are *sensors* 2.active smart textiles can sense the stimuli from the environment and also react to them, besides the sensor function, they also have an *actuator* function finally, 3)very smart textiles take a step further, having the gift to adapt their behaviour to the circumstances. So two components need to be present in the textile structure in order to characterize them as smart textiles; a sensor and an actuator. The traits start with a controlling part which drives the actuator on the basis of the signals from the sensor. intelligent character of the textile material can be introduced at different strategies. It can occur at fibre level which is very tiny measurments, a coating can be applied, other threads can be added to the textile material. The traits of smart textiles will be achieved only when the sensors

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and all related components are entirely converted into 100% textile materials. Salient aspect of challenges are technical considerations, concepts, materials, structures and treatments of the processing materials. So the factors needed to be on accounts are flexibility, water for laundry washing, resistance, durability against deformation, radiation, etc. As most signals are being transformed into electric ones, electroconductive materials are very important for this textiles. According to functionalities, smart textiles can be classified in five groups: sensoring, data processing, actuation, communication and energy. At the moment, most progress has been achieved in the area of sensoring and it helps to measure parameters like temperature ,biopotentials: cardiogram, myographs, encephalographs , acoustic: heart, lungs, digestion, joints , ultrasound: blood flow , chemical, blood pressure, IR radiation, spectroscopy , odour, sweat ,mechanical skin parameters , electric (skin) parameters. Some of these parameters are cardiogram and temperature. Nevertheless, permanent monitoring are also used for these traditional parameters . Also diagnosis can be a lot more accurate. Apart from the actual measuring devices data processing is a another used method. There are numerous data collection processes with multiple complex interrelationships with time. Actuation is another aspect, which consist of drug supply and physical treatment. Sensors can be divided into active and passive sensors [65]. Passive sensors require an external power source, while active sensors are able to convert the input energy into a measurable difference of potential. Conductive fibres and structures made from them are considered as passive sensors. Active sensors can work based on piezo-electric effects. Most of these conductive fibers or yarns are produced by applying conductive materials such as silver, copper, polyaniline , or other conductive polymers on polymer fibers and yarns by surface coating or electroplating techniques. Because of the irregularity of the fiber and yarn surface, the process may not lead to fully homogeneous coating,

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and therefore, the resistivity of the yarns will depend on the location of the measurement contacts [28]. This strategy also can be applied to filaments and yarns containing conductive particles such as carbon. The extent of these particles dispersed in the polymeric matrix and the formation of clusters can also create variations in the electrical resistance of the yarns. Electro-conductive fibres are very vital for a variety of functions in smart textiles: antistatic applications, electromagnetic shielding (EMI), electronic applications, infra-red absorption, protective clothing in explosive areas, etc. A set of fibres, yarns or fabrics separated one way or another can be considered as a double electrode system. Such a system can be used to detect water. The presence of water will be reflected in an increase of conductivity between the two electrodes. This increase will be bigger when the water contains salt. The reaction of such a textile sensor (i.e. resistance as a function of time), consisting of two conductive yarns.

The main area of smart textiles that has resulted into commercial products has been directly related to wearable electronics and monitoring sensors for healthcare and sports performance. [66]. People can use these smart textiles required for monitoring their health. Similarly, in sports and leisure activities, sensors can provide feedback on the heartbeat and breathing rate or even muscle activities, which is vital information to optimize training [67] Smart textiles are also widely used in the protection market, where the need for performance is often as important as the need for comfort. By integrating heating or thermoregulating materials within the worker's uniform, it is already possible to reduce their bulkiness while improving the overall comfort[67]. Smart textiles have applicable sectors such as transport, home textiles, construction, and fashion. With expansive research directed towards new topics such as energy harvesting textiles. Another form of conductive heating garments come in various forms: nonwovens, knits, wovens, embroideries, etc. They all use the same principle to dissipate heat when they are powered: the

Joule effect. In order to measure how much heat is generated by the heating garment, thermocouples have been used. The signals depend on the conductive element's dispersion, the choice of the position of the thermocouple on the heated surface will greatly impact the result obtained. Another form of smart textiles, cooling garments which are more complex and usually present a level of integration lower than the conductive heating textile. The reason behind that cooling garments are based on water or air circulating within small tubes inserted between two textile layers. The demands of the design of smart textile-based products that are attractive and pleasurable to wear by virtue of an appropriate blend of form and function. A key factor in the adoption of smart textiles and wearable electronics, in combination with the overall clothing comfort and appearance, is the design and usability of the technology user interface. So its important for designers and technologists must therefore work with older participants, to capture and understand their real user-needs and aspirations.

CHAPTER III

EXPERIMENTAL TECHNIQUES

Forcespinning

In Forcespinning, identification of process parameters vital because they influence fiber morphology and production. Fiber morphology represents several factors such as diameter, pores, formation -of beads- Previous works showed that these factors are determined mostly by viscosity and surface tension of the solution, as the elongation of fibers are dependent on them. The solution viscosity and surface tension primarily dependent on concentration of solution and polymer's average molecular weight_(Mw). Spinneret to collector distance, relative humidity (RH) temperature controls the solvent evaporation rate to generate fibers. The effective combination of these controllable factors can yield homogenous fiber otherwise bead formation are significantly present in fiber morphology.

Scanning Electron Microscope (SEM)

Scanning electron microscope, SEM (Carl Zeiss, SigmaVP)) was used to observe the morphology of collected fibers. The samples were sputtered with gold before examination. Five SEM images at the same magnification were used to determine the fiber average diameter.
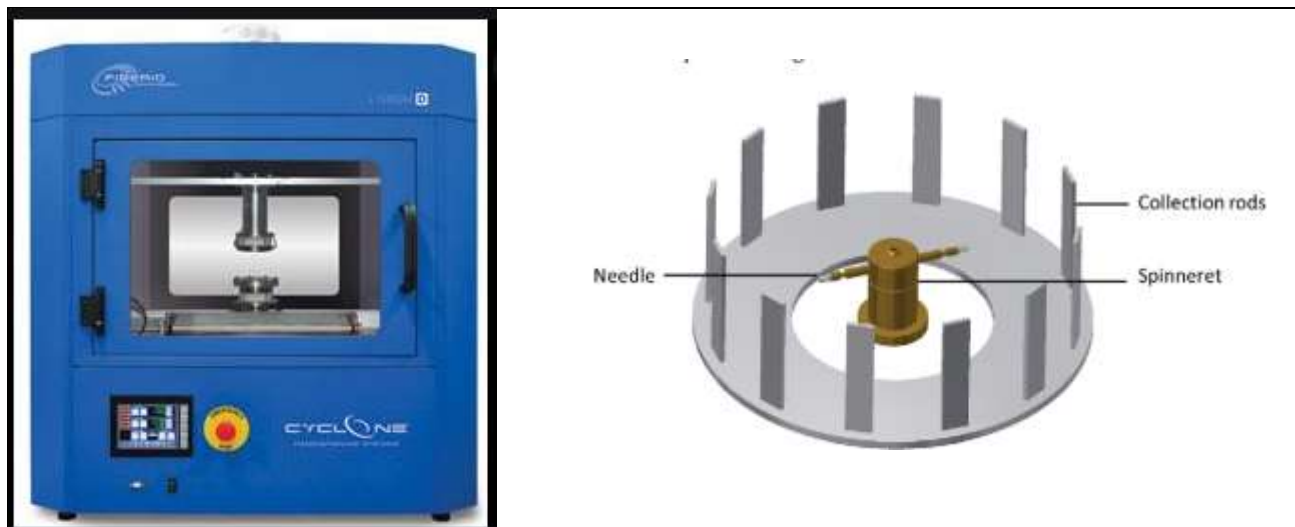
Figure 6: Forcespinning® machines (Cyclone) setup & mechanism of making fiber

Fourier Transform Infrared spectroscopy (FTIR)

FTIR spectroscopy offers analytical opportunities in academic, analytical and forensic labs. It covers simple compound identification to process and regulatory monitoring, chemical applications, especially for polymers and organic compounds. FTIR stands for Fourier transform infrared. When IR radiation is passed through a sample, some radiation is absorbed by the sample and some transmits through. The resulting signal at the detector represents a molecular 'fingerprint' of the sample. The usefulness of infrared spectroscopy is that it can cause different chemical structures produce different spectral fingerprints, The FTIR record information about a material placed in the IR beam. The Fourier Transform results in spectra can be used to identify the material. An FTIR spectrum arises from interferograms being analyzed and proved spectra. Patterns in spectra then identify the sample,as molecules shows particular IR fingerprints. With the FTIR configured to use a specific sampling device, the spectrometer can reveal different structures.
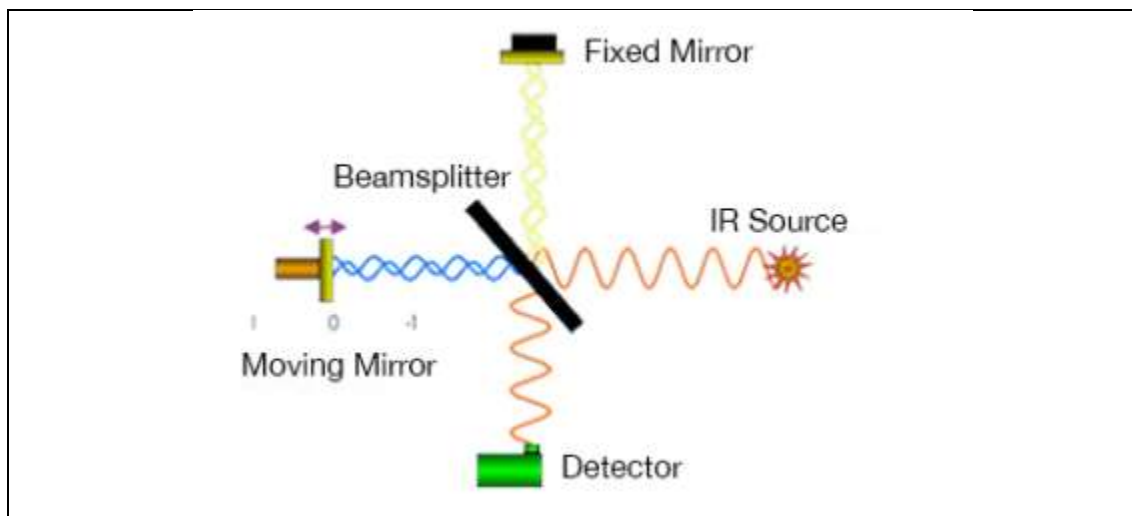
Figure 7: FTIR Working Scheme

Thermogravimetric analysis (TGA)

In Thermogravimetric analysis (TGA) continuously measures mass while the temperature of a sample is changed over time. Mass, temperature, and time are considered primary parameters in thermogravimetric analysis while many additional measures may be derived from these three base measurement. A thermogravimetric analyzer includes precision balance carrying sample pan located inside a furnace. The temperature is generally increased at constant rate or different rate depending on the applications to incur a thermal reaction. The thermal reaction may occur under a variety of atmospheres including: air, vaccum inert gas, gases, corrosive gases, carburizing gases, vapors of liquids as well as a variety of pressures. The thermogravimetric data are used in a plot of mass or percentage of initial mass on the y axis versus either temperature or time on the x-axis. It is called TGA curve. The first derivative of the TGA curve is called the DTG curve.
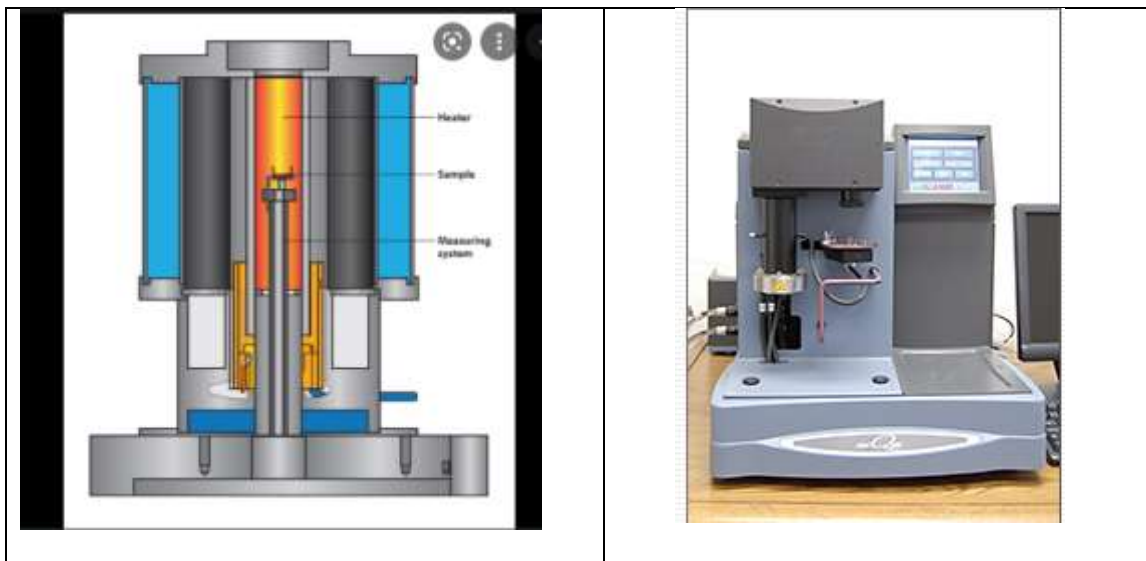
Fig 8: Thermogravimetric analyzer (TGA) component parts

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) calculates the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature. Generally, the temperature program for a DSC works in a way so that sample holder temperature increases linearly as a function of time.

The reference sample should have a controlled heat capacity over the range of temperatures to be scanned. The basic principle works here is that when the sample undergoes a physical transformation, more or less heat will need to flow to it than the reference. It is because of equilibrium needed to be maintained depending on whether is exothermic or endothermic. By observing the difference in heat flow , it can measure the amount of heat absorbed or released during such transitions.

Contact Angle Measurement

Contact angle is an angular measure of wetting of a solid by a liquid. It is geometrically defined
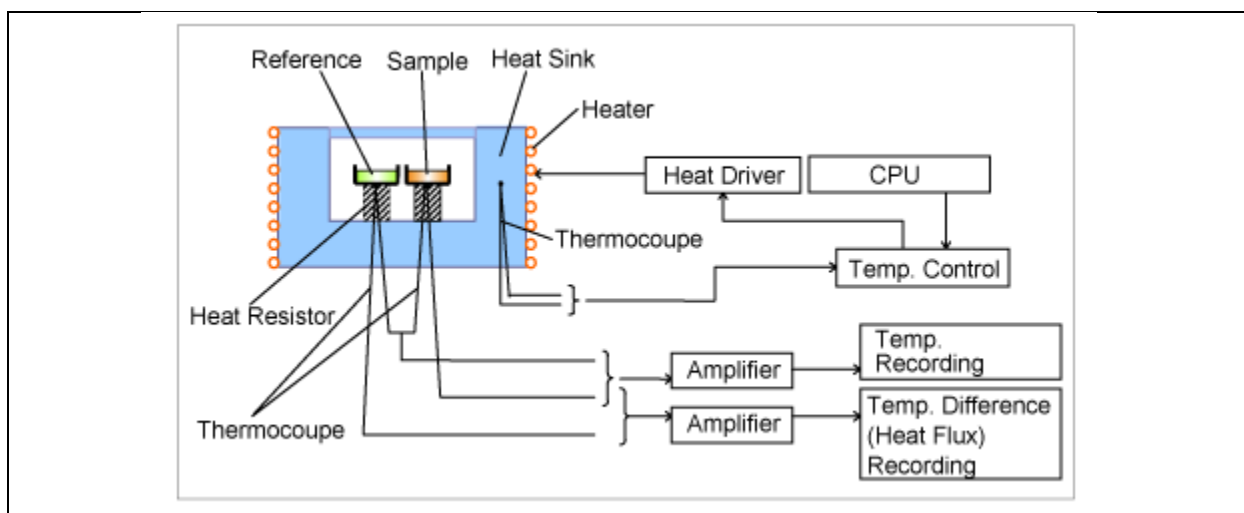
Figure 9: Block Diagram of Heat Flux DSC

as the angle formed by a liquid at the three-phase boundary. There are three different forces acting on this three-phase contact point between solid, liquid and gas, or in some cases solid, liquid and liquid. Contact angles can be divided into static, dynamic and roughness corrected contact angle. If the angle is more than 90º, then the material is hydrophobic and other type of material is hydrophilic.

X-Ray Diffraction (XRD)

XRD is a non-destructive test method which is used to determine the structure of crystalline materials. XRD analysis is used to identify the crystalline phases present in a material to further reveal chemical composition Identification of phases is achieved by comparison of the acquired data to that in reference structures. It is highly used for evaluating minerals, polymers, corrosion products, and unknown materials. In most cases, the samples analyzed by powder diffraction using samples prepared as powders. The characteristics used to determine in XRD are structural properties, lattice parameters, strain grain size, epitaxy phase composition, preferred orientation, measure thickness of thin films and multi-layers, atomic arrangement etc.
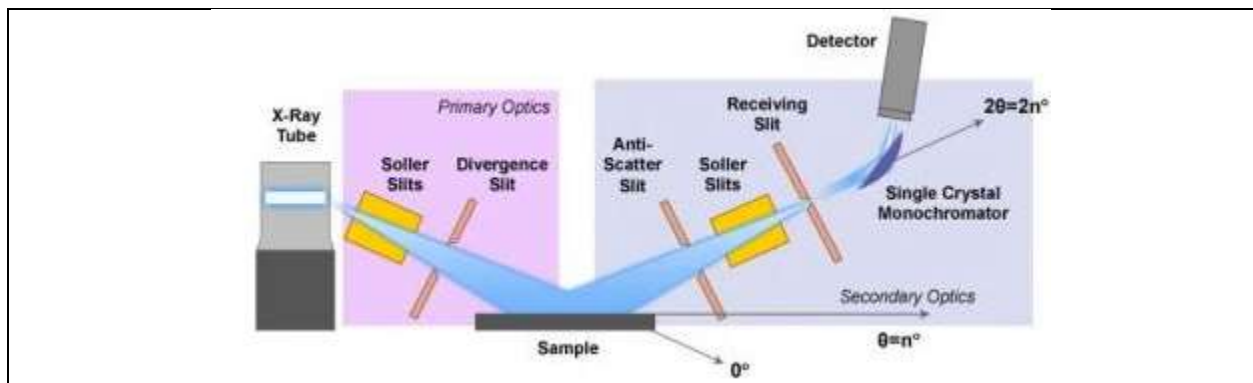
Fig 10: XRD analysis schematic mechanism

Photoluminescence Emission Spectroscopy & Excitation Spectra

Photoluminescence is implemented to characterize the optoelectronic properties of different materials. In the device, electrons are excited from the valence to the conductance band of the material by a laser with an energy larger than the bandgap. The photoexcited carriers relax and then spontaneously recombine with holes in the conduction band. The excess energy is emitted in the form of wave. By analyzing the spectrum of the emitted wavelength, the material's response in terms of intensity is measured. This gives data like the band structure, the bandgap

width, the relative light generation efficiency, the quality of the material etc. Additional

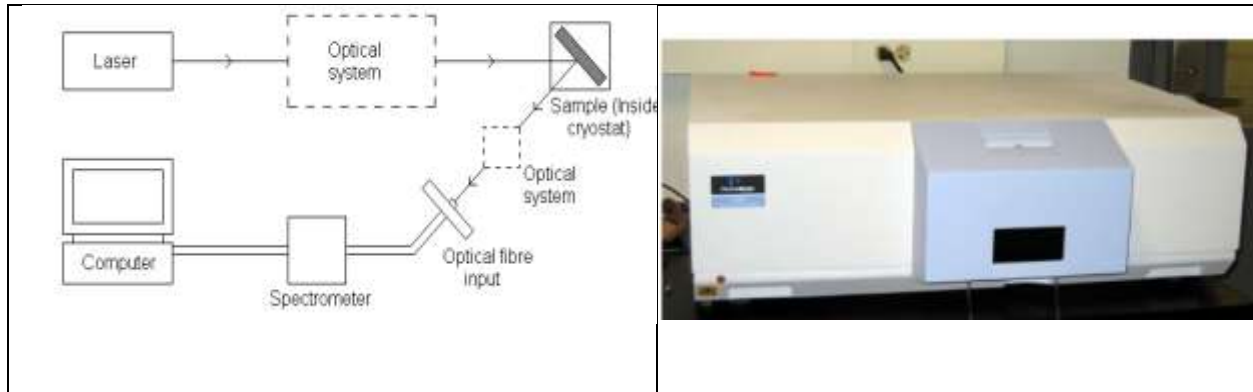information can be attained by controlling the sample's environment.

Fig 11: Diagram of Photoluminescence Spectroscopy setup & image of the instrument

CHAPTER IV

METHODOLOGY

Materials

Poly[4,4′-methylenebis(phenylisocyanate)-alt-1,4-butanediol/di(propyleneglycol) /polycaprolactone] which is a methylene-diisocyanate (MDI) polyester/polyether Polyurethane (PU) is purchased from Sigma-Aldrich. Chemical Structure of the selected Polyurethane is given in Fig.1. N,N- Dimethylformamide (DMF) which is used as solvent for the experiment also purchased from Sigma

ForcespinningTM Setup

Fig 2 shows simple schematic diagram of forcespinning process. 2 mL of solution was centrifugally forced out with rotating spinneret on which 30 gauge 1/2 inch regular bevel needles were mounted. Rotational speed is varied for each specific concentration to figure out the most yield or production. The run time for fiber production was between 5 and 7 minutes, and 5 runs were necessary to obtain a fine fibrous mat of each concentration. A 8 pillar collector system were used to deposit fiber where collectors were stayed 5-7cm from the tip of the needles. After collection, the fibers were stored with desiccators for humidity control

Solution Preparation

PU is dissolved into DMF with the concentration of 14wt%,15wt%, 16wt% and 17wt%. To create a homogenous solution, the mixture is stirred with magnetic stirrer betweenfor 24 and-48 hours by placing it on oil bath at 104-1090C. The mixture is kept at scintillation vials and cooled down until room temperature before using it in the forcespinning machine.

Experimental design of PU Production

Polymer concentration and angular speed are considered as vital process parameters in forcespinning process [61] [46][47]. Different concentrations of PU ranging from 5 wt% to 20 wt% were used in an interval of angular speeds from 2500 to 9000 rpm for the fiber production. in the experiment,. The first parameter considered for the selection of the systems was the feasibility to get enough fibers for the fabrication of fibrous mat. Once the systems were selected, the second parameter evaluated was the fiber diameters. Among them, the above mentioned 4 concentrations are found feasible because only they can give enough fiber deposition in the collector with which nonwoven homogenous fibrous mat can be build. For 5 wt% to 12wt%, no fibers were generated from forcespinning which were tried with different angular speeds ranging 2500-9000 rpm (with 500 rpm increment from 2500 rpm). Other concentrations provided very negligible amount of fibers within the mentioned angular speed range. These experiments were conducted in 50-55RH and 70-77F, as these were the most usual conditions found during the experiment time in the lab. For 4 selected concentrations and in the given usual ambience, best angular speeds for each were figured out in regards of feasibility. This is how PU fiber generation is optimized in the experiment. The equation which estimates the production of fiber under operating conditions is given below,

$$np = W/TS \times 100$$

W is the weight of fiber collected per run and TS total solids contained in 1 ml of solution. Here total solid is the amount of polymer present in 1 ml of solution assuming 100% of transformation of total solid into fiber.

Characterization

The nanofibers were characterized by Scanning electron microscope (SEM), Water Contact Angle Test and Fourier transfer infrared spectroscopy (FTIR) to investigate the fiber morphology and transmittance properties of the fiber.

SEM Characterization

Scanning electron microscope, SEM (Carl Zeiss, SigmaVP)) wasis used to observe the morphology of collected fibers. The samples were sputtered with gold-palladium before examination. Five SEM images at the same magnification were used to determine the fiber average diameter. The images were processed by ImageJ software. At least 20 measurements were taken from each image in order to have 100 measurements in total. The mean value and standard deviation were determined with the help of MINITAB® software.

Contact Angle Measurement

The contact angle measurement were performed with Kyowa Interface Science Co. Ltd., Model DM-CE1. Using a syringe with 30 gauge needle (I.D 140 μm), a drop of about 3 μL of deionized water was placed onto the PU mat deposited on a glass slide. Then, an image was captured with a digital camera. A clear image showing droplet contour and baseline was visible with assistance of a light source covered with a diffuser which was kept behind the substrate. For each sample regarding a particular concentration, 10 pictures were taken; from each picture 10 measurements were evaluated. So overall, for each sample 100 measurements were assessed by

senile drop method with ImageJ. The drops were released with the contact of fibrous mat. Average values were used in wettability analysis.

FTIR Characterization

The Fourier Transform Infrared Spectra of the fibers membrane were obtained by using 133 VERTEX 70v FTIR Spectrometer (Bruker) in Attenuated Total Reflection (ATR) mode. The transmittance data of the nanofiber samples were recorded from 450 cm^{-1} to 4000 cm^{-1} wavelengths

TGA Characterization.

TGA The thermal properties were evaluated through thermogravimetric analysis (TGA) (TA Instruments, Q400).To perform the TGA, the sample was heated from 30C to 600C under a nitrogen atmosphere, at a heating rate of 10Cmin−1.

DSC Characterization

The device used for the experiment is Differential Scanning Calorimetry (DSC) (TA Instruments, Q200). Regarding the DSC, the heating was carried out from −70 to 200C at a speed of 10C min−1, the sample was isothermally maintained at 200C for 2 minutes and then cooled down at the same rate to −70C. A second heating cycle under the same conditions was conducted.

<div align="center">

Synthesis of Nanoparticles

</div>

Mn doped Zinc Germanate (Mn: Zn_2GeO_4)

Mn doped Zinc Germanate (Mn: Zn_2GeO_4) is a Luminescent material with bright and green emission. It was made from Biphasic reaction to make it Water and DMF dispersible. It is capable of excellent Green upon irradiation with 254 nm UV light. The particle is found cost-effective and

environmentally benign phosphors. Potential Applications are: bioimaging, solid state lighting, *in vivo* & *in vitro* imaging and security.

Chemical components are trialed to find Optimization of 2.0 mmol of $Zn(NO_3)_2$ with 1 mmol of GeO_2 and 0.005 mmol .The amount and procedures are given below to make Mn doped Zinc Germanate (Mn: Zn_2GeO_4) Nanoparticles:

Zinc Nitrate Hexahydrate 1mmol = 0.298 g / 5 mL H_2O

Germanium Dioxide (GeO_2) 2mmol = 0.2046 g / 5 mL H_2O

(To make GeO_2 stock ammonia is added in limited amount so that it can dissolve)

Manganese nitrate hydrate = 0.5 mL per reaction (Stock 0.0179 g in 10 mL H_2O)

1. Mixing these three solutions and adding Ammonia to make pH10

2. Stiring the solution for 30 minutes. It will be called part A stock

3. Take 10 ml Toluene this to Teflon part of hydrothermal reactor

4. Adding 2 ml oleic acid and 1ml oleyl amine to the Teflon part

5. Adding part A stock to the Teflon part

6. Keeping it at 120 °C in the oven for 14 hours.

7. Washing it with Acetone and collecting the NPs .

Cr doped Zinc Gallate (Cr: $ZnGa_2O_4$) Nanoparticles (Red)

This nanoparticle gives luminescence with Red emission .Red emission UV excitation at 254 nm. This is also Water and DMF dispersible. *Ex situ* excitation making *in vivo* bio-imaging

possible for this nanoparticle as well. Trial synthetization were run to find the Optimization: 1.0 mmol of $Zn(NO_3)_2$, 1.996 mmol of $Ga(NO_3)_3$ and 0.004 mmol of $Cr(NO_3)_3$

Potential Application: medical diagnostics and night-vision materials (for example, emergency signs and displays, light-emitting devices and optical probe in bioimaging

The amount and procedures are given below to make Cr doped Zinc Gallate (Cr: $ZnGa_2O_4$) Nanoparticles (Red)

Zinc Nitrate Hexahydrate 2mmol = 0.5949 g / 3 mL H_2O

Gallium Nitrate hydrate 2mmol = 0.726 g / 3 mL H_2O

Chromium nitrate nonahydrate = 0.5 mL / per reaction (Stock 0.04 g in 10 mL H_2O)

Ammonium Nitrate 4 mmol = 0.32 g / 5 mL H_2O

Urea 25 mmol = 1.5 g /5 mL H_2O

1. Mixing these five solutions

2. Stiring the solution for 30 minutes. It will be called part B stock

3. Take 10 ml Toluene this to Teflon part of hydrothermal reactor

4. Adding 2 ml oleic acid and 1ml oleyl amine to the Teflon part

5. Adding part B stock to the Teflon part

6. Keeping it at 220 °C in the oven for 10 hours.

7. Washing it with Acetone and collecting the NPs.

Fig 12: a) Hydrothermal Reactor parts b)Hydrothermal Reactor c) Oven d) Centrifuge m/c

PU Fiber and Nanoparticles Integration

Forcespinning with Nanoparticles

Nanoparticles (NP) produced from each reaction through reactor were dissolved into the DMF and Stir it with magnet to dissolve properly with time. Then, PU pellets were added in the DMF Solution. The overall solution was put into heat at oil bath at 104-109C which eventually will be used to forcespun to fabricate fiber. Pu pallets were added to make 15,16 and 17 wt% of solution in DMF.

Ex-situ Loading

There are two ways that Nanoparticles are dissolved into solution of Water and DMF by stirring. Produced Fiber Mat are submerged into the solution for 24-48 Hours. PU fiber mat under solution of 40 percent DMF and 60 percent water so that with time the nanoparticles will try to accumulate on fiber. DMF was added to create some scratch and roughness on the fiber mat surface that pave a way for nanoparticles to stay over it.

In another effort, Nanoparticles placed over Aluminum (Al) foil. Al foil is pressed over the fiber and A card is used to scratch over the foil to make the nanoparticles substantially being attached to PU fiber mat.

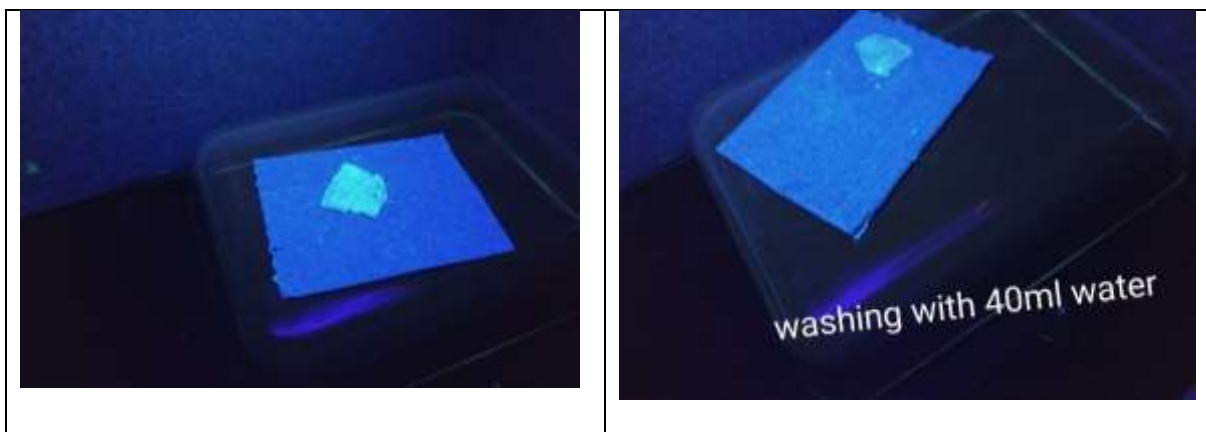Fig 13: Fiber mat submerged into Water-DMF-Nanoparticle Solution

Fig 14: Nanoparticles scratched over Fiber mat

XRD Characterization

XRD patterns of the nanoparticles and fine fibers were extracted with a Bruker D8 Advance X-ray diffractometer (XRD) with Cu Kα1 radiation ($\lambda = 0.15406$ nm). The XRD data was obtained by a scanning mode of 2θ, ranging from 20◦ to 80◦, with a scanning step size of 0.04◦ and a scanning rate of 2.0◦ min^{-1}

Photoluminescence Emission Characterization

The excitation and emission spectra of the nanoparticles and fine fibers were extracted by an Edinburgh Instruments FLS980 fluorimeter system equipped with a Xenon (Xe) lamp and a TE-cooled photo-multiplier tube (Hamamatsu, Model R928P) for emission detection. The excitation and emission spectra were corrected for determining the spectral sensitivity.

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CHAPTER V

RESULT AND DISCUSSION

Morphology of Nanofiber Membrane

In Figure 3, SEM images of systems corresponding to the concentration of 15 wt%, 16 wt% and 17 wt% PU and each concentration associated with 4000,5000,6000,7000 rpm are given along with their mean diameter and diameter distribution. These systems were selected using the criterion described in the experimental design section. In the Table 1, the condition associated with the fiber production are shown.

Table 1. shows the process yield of each system. 16wt% PU forcespinned with 7000 rpm gives the highest yield and 15 wt%-5000 rpm system gives the lowest. Among the presented combinations, a general observation can be seen that a combination with lower rpm gives low fiber yield and a combination with higher rpm tends to transform higher amount fiber from the polymer-solvent solution. For 4000 rpm which is the lowest rpm in our experiments, 15wt%, 16 wt% and 17 wt % PU gives respectively 12.24%,12.29% and 11.59% process yield. These are almost the lowest percentage of transformation of fibers. Similarly except for 15 wt%, system with 7000 rpm gives very high production of fiber. 16wt%-7000 rpm and 17wt%-7000 rpm combinations give respectively 37.2% and 32.95% process yield.

A relevant result was found in the case study of Padron et. Al.[high rpm high yield paper]. In their experiment with BEH-PPV fiber production, it is found that if critical angular speed in not achieved, the solution will produce fiber instead of beads. When the velocity is significantly lesser than this speed, the hybrid nanofibers were able to be forcespun at higher speeds with high yields at 5 and 10 wt %. Among the different concentrations, PU 17wt% can be observed as the most productive. For 5000,6000 and 7000 rpm, process yields are respectively 28.87%, 31.6% and 32.95%; all yields are as high as around 30The tests conditions were kept at 51-56RH and around 75F. Relative Humidity (RH) was comparatively high. Under 30RH fibers weren't generating and around 50RH measurable amount of fibers been yielded for all experimented concentrations and rpm. The possible explanation for good fiber production at higher humidity is due to lower rate of evaporation [68]. The low rate of evaporation allows fiber more time for stretching out and continuous formation along the circular path paved by collectors. Spinnability has shown improvement with increase of concentration. For 5wt%-13wt% PU concentration fibers weren't produced, lower spinnable concentration threshold could be affected by the shear stresses applied to the forcespinned polymer jet. The reason of a concentration threshold below which spinning is no longer possible can be attributed to entanglement concentration c_e ((Pham, Sharma, & Mikos,2006) or critical chain overlap concentration,c^*.The average fiber diameter is found to be from 0.23485±87.47 to 0.311113±90.26.

Table 1: Fiber Sample Weight, Avg. Diameter, Standard Deviation and Process Yield

Concentration & RPM	Weight of sample(gm)	Humidity	Temperature	Avg Dia	Standard Deviation	Process Yield
15 wt% and 4000 RPM	.0204	54	75	0.238068	77.30	12.24%
15 wt% and 5000 RPM	.0147	54	75	0.311113	90.26	8.82%
15 wt% and 6000 RPM	.0356	53	73	0.3104	89.76	21.37%
15 wt% and 7000 RPM	.0306	53	73	0.23485	87.47	18.37%
16 wt% and 4000 RPM	.0221	55	73	0.26102	95.88	12.29%
16 wt% and 5000 RPM	.0421	55	75	0.253315	93.97	23.42%
16 wt% and 6000 RPM	.0288	56	73	0.268537	79.30	16.01%
16 wt% and 7000 RPM	.0669	54	73	0.26715	96.54	37.2%
17 wt% and 4000 RPM	.0224	56	75	0.253763	80.12	11.59%
17 wt% and 5000 RPM	.0558	55	75	0.28434	104.515	28.87%
17 wt% and 6000 RPM	.0611	52	75	0.26905	116.19	31.6%
17 wt% and 7000 RPM	.0637	51	75	0.27493	87.44	32.95%

Corresponding diameters for all systems remain pretty much close to each other. For 16wt% concentration, measured fiber diameter remains most consistent for the 4000-7000 rpm range from 0.253315±93.97 to 0.268537±79.30. Standard deviation values shows mostly a

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tendency to increase with rpm. The evaluated fiber diameters are[49],[51],[53]fine compared to the fiber diameters those are generated through electrospinning process.

In Table 2, Quartile 1(Q1) and Quartile 3(Q3) of fiber diameter distributions for the systems obtained to different PU concentration are presented. From the IQRs presented in the Table 2, the range between Q1 and Q3 remains closed to each other. The IQ values are between .10050-.12975. Comparative homogeneity in the distribution of fiber diameters is seen here. It can be explained with the structure of the polymer which is a multiblock polyurethane containing poly-caprolactone(PCL). This polymer structure has high degree of chain entanglement and physical crosslinks [69]. This characteristic leads to high viscous force to overcome during forcespinning and thus tries to preserve the range of diameters of centrifugally spun jet.

Concentration wt% (RPM)	Quartile 1 (nm)	Quartile 3 (nm)	IQR (nm)
15wt% (4000)	0.17300	0.28650	0.11350
15wt% (5000)	0.24700	0.36850	0.12150
15wt% (6000)	0.24325	0.37300	0.12975
15wt% (7000)	0.17050	0.28200	0.11150
16wt% (4000)	0.18900	0.31725	0.12825
16wt% (5000)	0.17950	0.30850	0.12900
16wt% (6000)	0.20875	0.30925	0.10050
16wt% (7000)	0.19725	0.31450	0.11725
17wt% (4000)	0.19725	0.31450	0.11725
17wt% (5000)	0.19750	0.30275	0.10525
17wt% (6000)	0.2163	0.3388	0.1225
17wt% (7000)	0.20775	0.33075	0.12300

Table 2: Fiber Diameter Distribution

By forcespinning method, fiber production is found significant when concentration range is within 14-17 wt% at usual lab condition. Fiber production for outside but close to that range is sparse and small in amount. In Fig 3. the fibers are observed as wavy, curly and long . It is because at higher concentration, PU fibers exhibit curly, wavy and straight structure. [56]As significant fiber production starts from 14wt% or high concentration range, all the samples show wavy appearance. For 15wt% sample, beads formation observed. Beads are undesirable segments in fiber structure as they reduce surface area to volume ratio. The observation is similar to Demit et. Al.[56] and Fong et. Al. [45]where it is found comparatively lower concentration exhibit bead structure. Another significant observation is fiber being fused with each other and overlapping on another.. Ghelich et Al. [48] made such observation when they electrospin PVA/NiO-GDC fibers which distance. This happens mostly due to lack of adequate solvent evaporation which could be caused by higher humidity and shortage of distance travelled by forcespunned jet The trapped solvents which doesn't get chances to vaporize usually diffuse out after the fiber has deposited and leads to fusion of the fibers. Kim et al [50] build a separator made of electrospun cross-linked poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-co-HFP) fibers. A less volatile solvent N-methyl-2-pyrrolidone (NMP) was selected as solvent so the deposited fibers weren't sufficiently dry enough and create fusion at contact point .
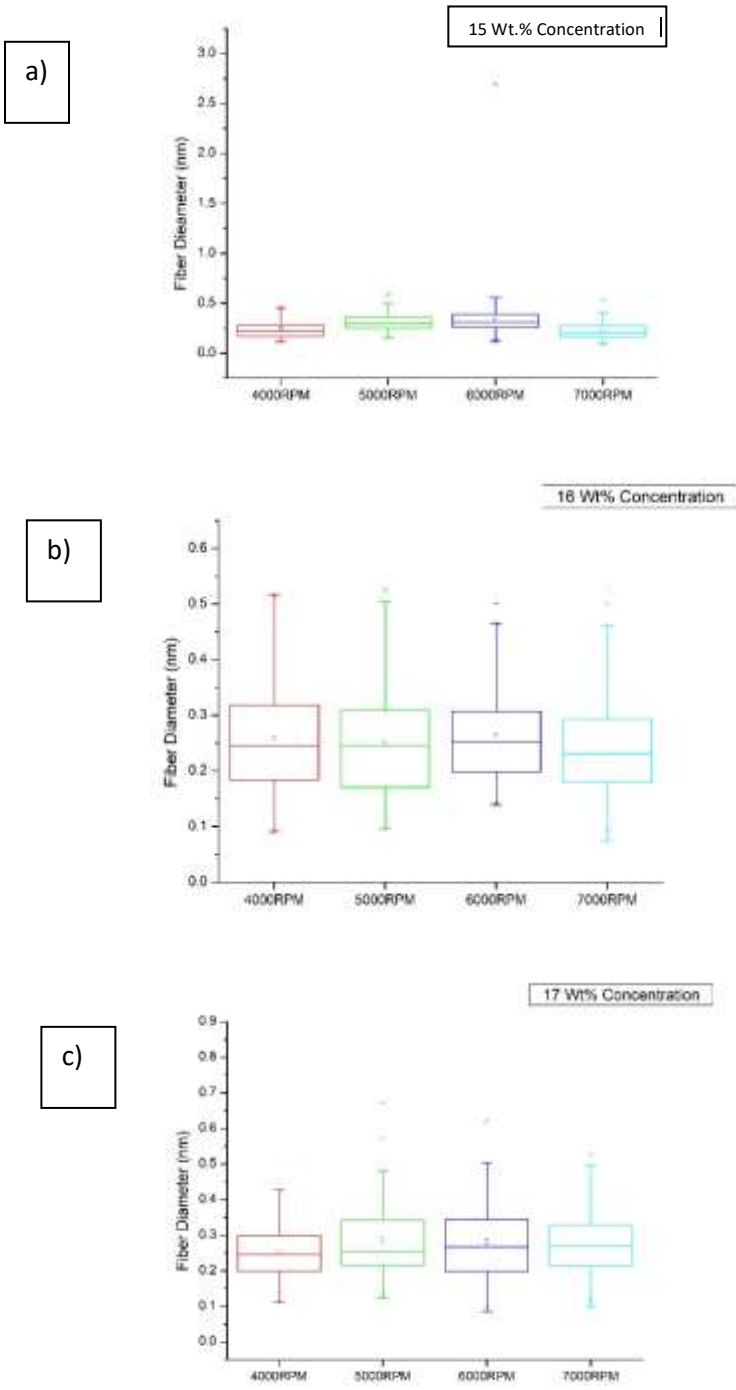
Figure 15: Box charts of PU fiber diameter as a function of angular speed applied to a)15 wt%, b)16 wt% and c)17 wt% Concentration. Boxes indicate the interquartile range (IQR) between Q1 and Q3, the upper and lower whiskers represent 1.5 times the IQR and the minimum value

of the distribution, respectively. The horizontal line is the median, the small square inside the box is the mean of the average fiber diameter.

FTIR Analysis

The spectrum revealed that TPU membrane absorption band at 3325 cm^{-1} was due to the N-H stretching vibration in the urethane group . – CH2– asymmetric stretching vibration creates
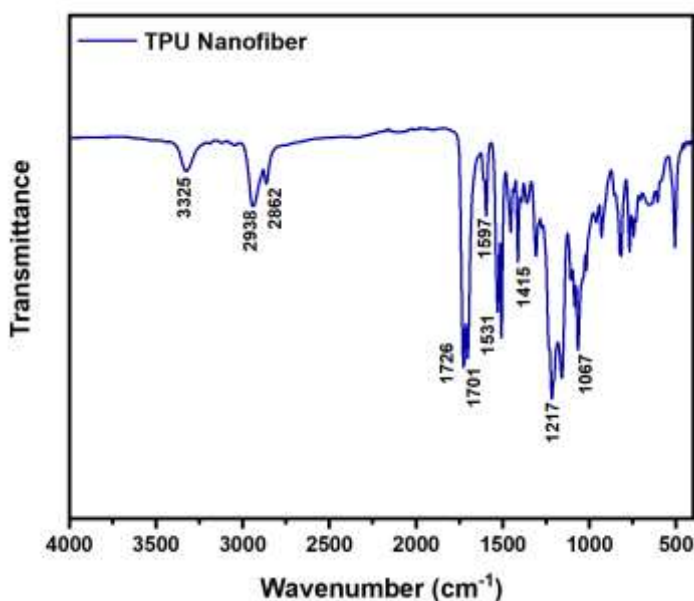

Figure 16: FTIR spectrum of TPU nanofiber.

absorption band of 1415 cm^{-1}, 2862 cm^{-1} and 2938 cm^{-1} [70].It can be observed at 1726 and 1701 cm-1 there are some sharp peaks. It can be explicated along with stretching vibration of the carbonyl group (C=O) in the amide while stretching at 1597 cm^{-1} caused by N-H group flexural absorption[71]. The band around 1067 cm^{-1} and 1217 cm^{-1} were characterized by C–O bond stretching[72].
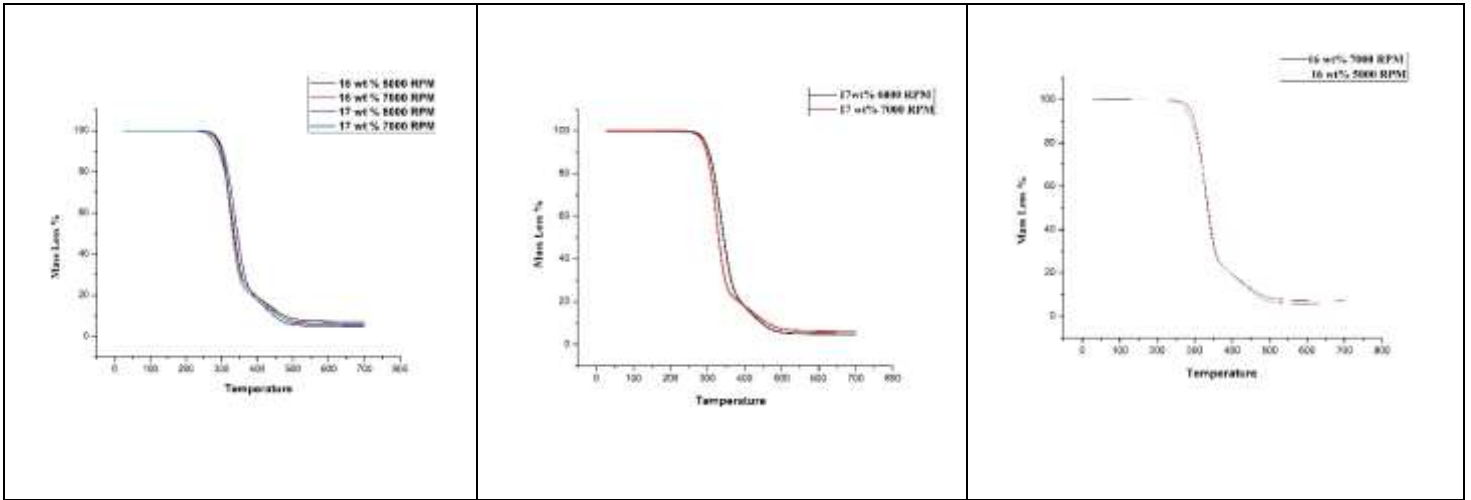
75

Thermal Characterization of PU

Figure 17: TGA Analysis of TPU nanofiber.

In TGA curve, single step polymer degradation is observed. The degradation occurs at 255-510C temperature range and the mass loss is very significant (92% mass loss). Thermoplastic MDI-based polyurethanes show comparatively early degradation in the range of 200C-300C due to low thermal stability. Lack of robustness in thermal stability is responsible for the cleavage of the urethane linkage, it decomposes at higher temperatures into a mixture of nitrile compounds (such as HCN) and polyols residue, and to the breaking of ester bonds in the macro glycol group.[28]The degradation onset is considered with 5% weigh loss from intact sample. 4 samples were tested for thermal property analysis, among them 16 wt%-7000 rpm shows degradation at earliest. In 200-380C range when around 75% of mass loss takes place, 17wt%-7000 rpm sample shows fastest degradation and 17wt%-6000 rpm sample is observed as most stable. For around 380-500C range, 17wt%-7000 rpm started to degrade most quickly and 16wt%-5000 rpm sample's mass loss rate become slowest. From the samples, rpm or concentration of systems doesn't seem to have any effect on polymeric degradation.
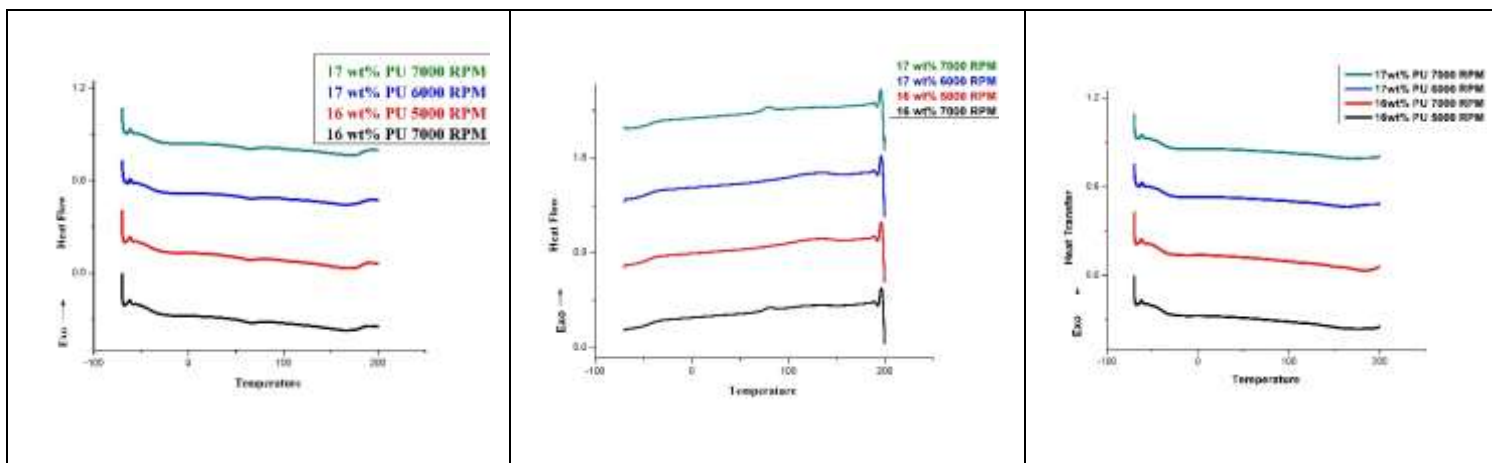
Figure 18:   DSC analysis of TPU nanofiber.

DSC curve shows here consist of 3 graphs, a heating curve followed by cooling curve and then a reheating curve. First heating curve gives glass transition temperature or T_g as -48C by an endothermic peak followed by a broad endothermic peak with maximum at around 160C(T_m or melting temperature) for all the samples. 16wt%-7000 rpm system shows highest melting temperature of 166C here. The MDI-polyether-ester urethane has soft segments are formed by the polyether-ester moieties and have low glass transition temperature, while hard segments derived from the aromatic di-isocyanates and develop a crystal phase stabilized by H-bonds. [52]Peaks in the 70–80◦C range have can be attributed to the interruption of urethanemacroglycol H-bonds at the interface of the microdomains and peaks in the 150–180◦C range to the disruption of urethane-urethane H-bonds. After cooling, the second heating curve reveals almost the same T_g for samples, 17wt%-6000 rpm sample having highest glass transition temperature and 16wt%-5000 rpm system having the lowest. Second heating curves lacks the peak in the 70–80◦C range typical of urethanemacroglycol H-bonds at microdomains interfaces, whereas it melting peak at T_m =160-178 suggests the presence of urethaneurethane H-bonds in the crystal phase. These differences can be clarified by hypothesizing that the cooling has restricted phase segregation between soft and

hard segments, thus decreasing the contribution of H-bond at the interphase with an amorphous phase richness.

Contact Angle Measurement

Contact angle measurements are representation of wettability of the material's surface. The liquid used in contact angle measurement is water. Water contact angle measurement mainly depends on the fiber surface morphology and chemical composition of the polymers. The average water contact angle for 14wt%,15wt%,16wt% and 17wt% PU samples were 107.49°,113.17°,113.77° and 113.02° respectively and standard deviation for these samples contact angles are respectively 4.492062732, 4.813465043, 0.716564877, 1.364364687. With higher concentration. the samples show more consistence in measurements. The hydrophobicity observed in the samples is related to the presence of polycaprolactone as part of the PU structure (PU) due to PCL has superhydrophobic property. Nguyen el. Al[62] showed the water contact angle for similar PU is 110° which is close to our observation.
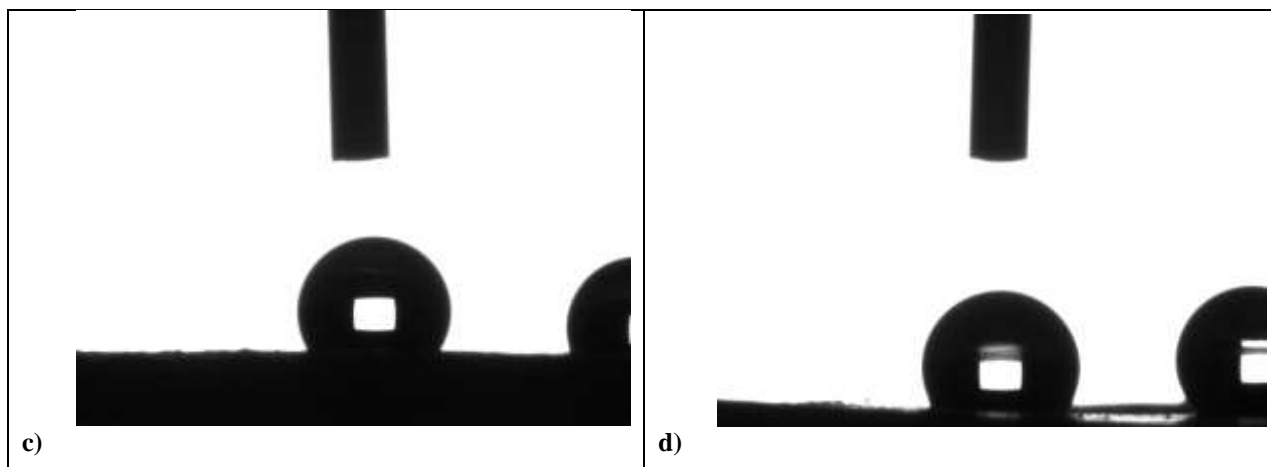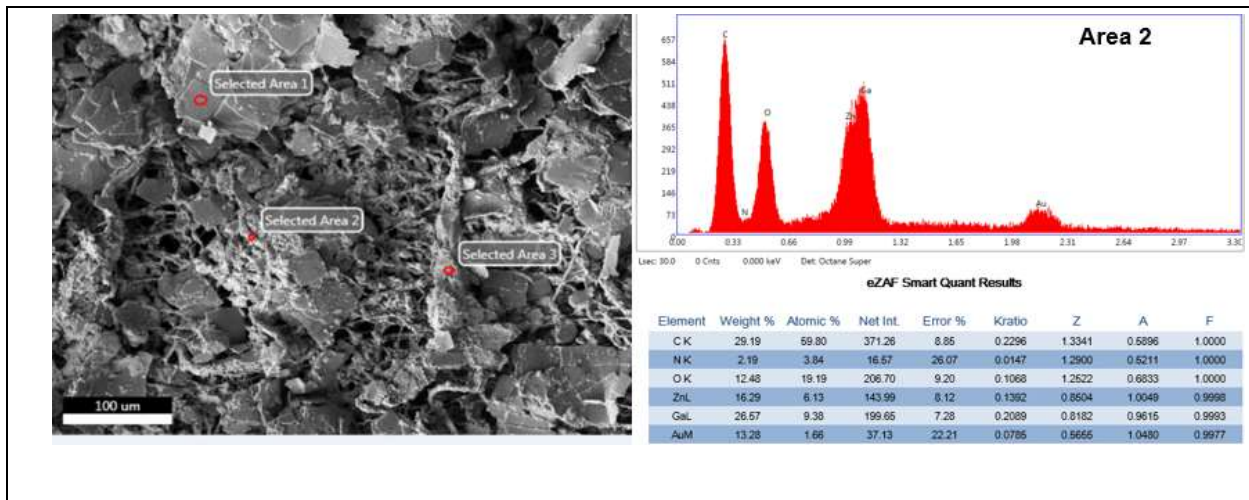

a)   b)
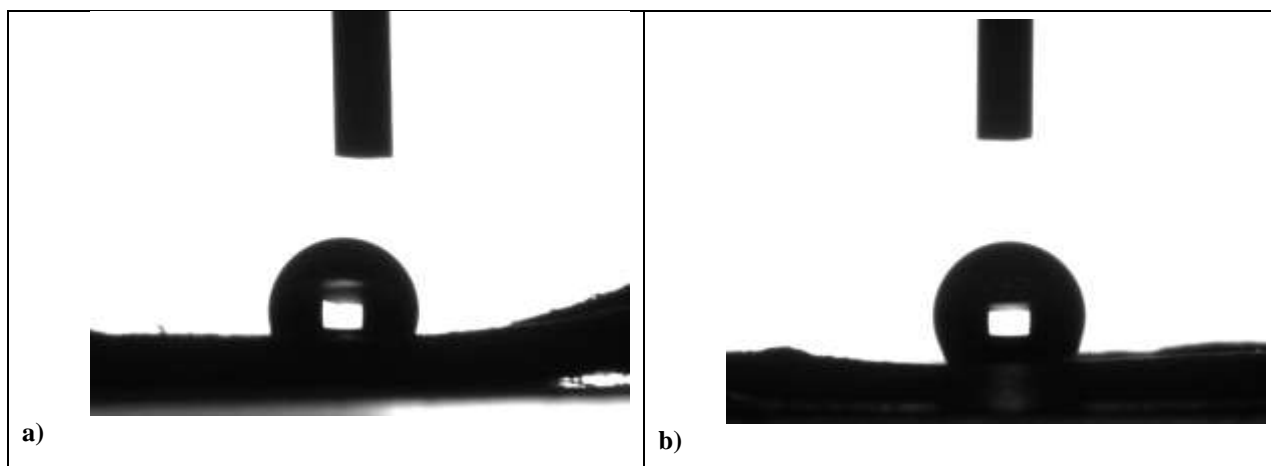
Figure 19: Photograph of water contact angle and water droplets on fibrous mat of a) 14 wt%
b) 15wt% c) 16 wt% and d) 17wt% of PU

Nanoparticles Incorporation in Fiber

With forcespinning method, nanoparticles incorporation in fiber wasn't found suitable.
Most of nanoparticles weren't loaded or lost luminescence into fiber matrix. Because of PU-
DMF solution being viscous, it was really hard to dissolve nanoparticles into the solution, with
time it get precipitated. Synthesized nanoparticles didn't have the required compliance solution
to retain it's consistency of producing fibers. They either get quenched or have effect on PU
structure, which didn't let fiber production.

As both Mn doped green and Cr doped red nanoparticles showed good solubility in
water, it can externally took place over fiber matrix when it was submerged into DMF-water
mixture. Presence of DMF helped to scar fiber in a way to place nanoparticles on fiber substrate.
The solution (10%, 20% and 40%) with increasing DMF gives better result and accruement of
nanoparticle over fiber surface. However, this ex-situ incorporation wasn't substantial as with
washing, most of the nanoparticles were taken away. This was obvious due to nanoparticles
strong solubility in water.

In another attempt, the nanoparticles were scratched over fiber, putting nanoparticles on Al foil at one side and place the side with fiber mat. The fiber mat can adhere with particles strongly in the process and showed better retention after washing (Fig:) than the previously mentioned method where mats were only submerged. SEM-EDS (Energy Dispersive X-ray Spectrometry) analysis of these mat showed well presence of particles. In green particle, the constituents O, Zn and Ge are showing their presence with characteristic peaks which are at .513, 1.012 & 1.188 KeV (Chart from www.EDAX.com). This can be seen in the Fig: Similarly, the constituents O, Zn and Ga (1.098 KeV) are showing their presence with characteristic peaks. The particles showed in the SEM images, are in agglomerated form, more research in the area could bring idea about the size of the particles and their orientation.

eZAF Smart Quant Results

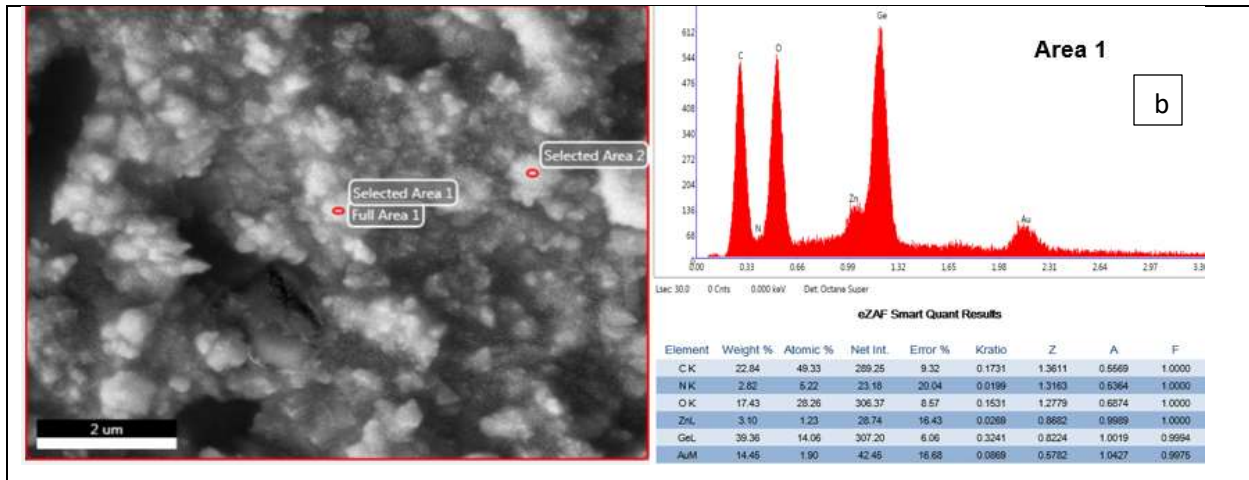| Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	29.19	59.80	371.26	8.85	0.2296	1.3341	0.5896	1.0000
N K	2.19	3.84	16.57	26.07	0.0147	1.2900	0.5211	1.0000
O K	12.48	19.19	206.70	9.20	0.1068	1.2522	0.6833	1.0000
ZnL	16.29	6.13	143.99	8.12	0.1392	0.8504	1.0049	0.9998
GaL	26.57	9.38	199.65	7.28	0.2089	0.8182	0.9615	0.9993
AuM	13.28	1.66	37.13	22.21	0.0785	0.5655	1.0480	0.9977

Fig 20: SEM EDS Characterization of a) Red Nanoparticle's and b) Green Nanoparticles
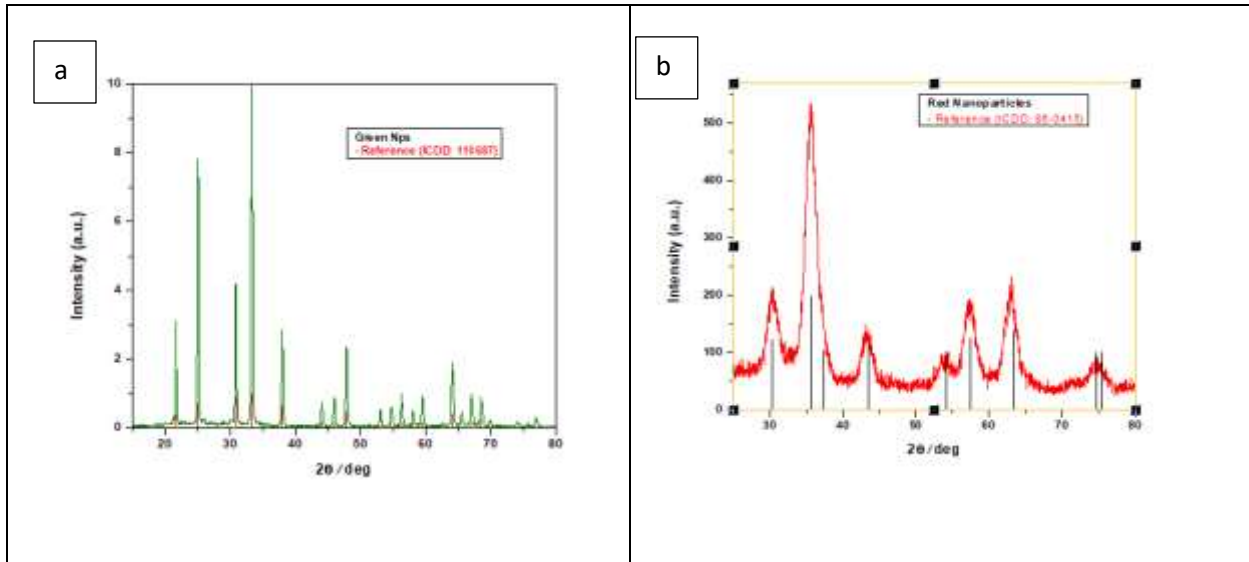

Fig 21: a) XRD analysis of Mn doped Green Nanoparticles & b) Cr doped Red Nanoparticles

XRD Analysis of Nanoparticles

The XRD patterns obtained was aligned and similar with the standard pattern of pure rhombohedral ZGO. Mn ion doping does not distort the basic ZGO structure. Based on the analogy of charge and size matching, Mn^2 is expected to be localized at Zn^{2+} sites. The crystal structure of Zn_2GeO_4 is well discussed by Chi *et al.*[73] ZnO_4 acts as a network modifier of ZGO and GeO_4 as a network former which can be attributed to the fact that Zn and Ge have a

coordination number of 4. No impure crystal phases of ZnO, GeO$_2$ or MnO$_2$ or other impurities were found .Mn^{2+} ions are doped into the ZGO lattice well. The sharp diffraction patterns indicate high crystallinity present in nanoparticles[74]

TGA Analysis of (Fiber-Nanoparticles)

For fiber with nanoparticles Thermal Degradation onset were found as 154.39 ℃ for Fiber-Green nanoparticles and 166.38 ℃ for Fiber- Red nanoparticles. It can be seen around 90% mass loss around 500℃ for green nanoparticles- fiber and 70% mass loss around 850℃ for red nanoparticles- fiber. Earlier, for pure Pu fiber TGA analysis were discussed, from there negligible shift for addition of green nanoparticles can be seen but better mass retention for red nanoparticles are observed.
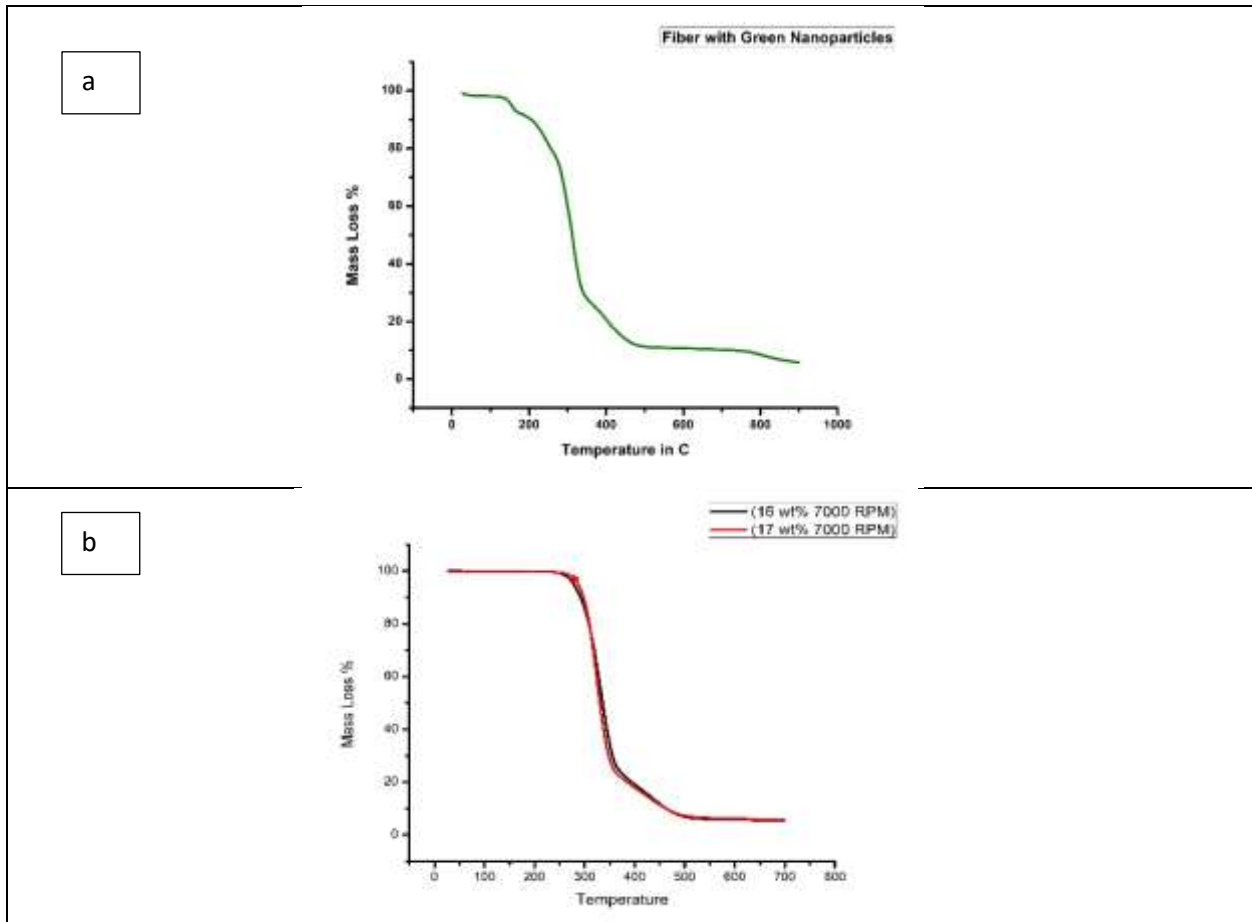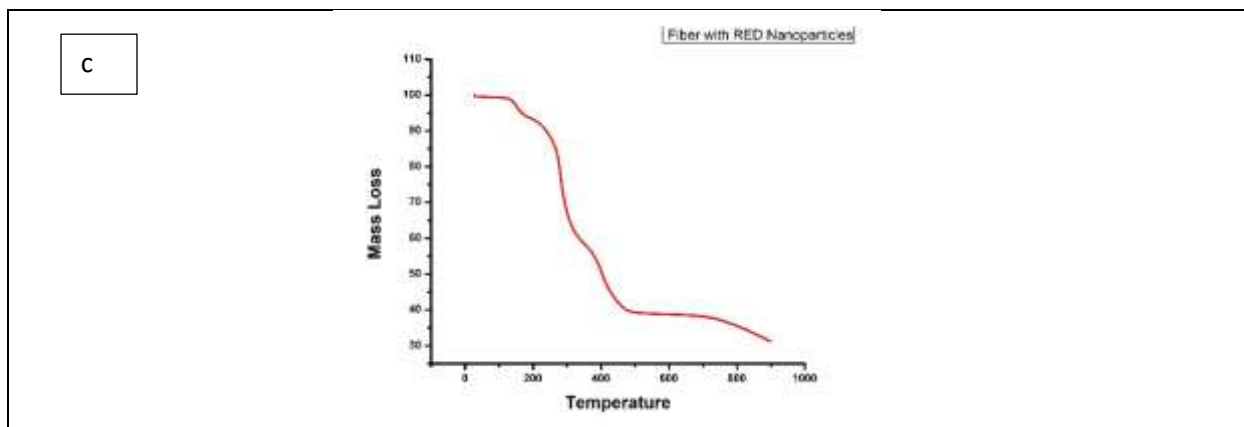
Fig 22 a) TGA analysis for Fiber-Green Nanoparticles b) Only fiber c) Fiber-Red Nanoparticles

Photoluminescence Emission Spectroscopy (PL)

From Photoluminescence Emission Spectroscopy analysis, Emission spectra was found for green nanoparticles at 305 nm Green Particles. It can be seent there is a Broad emission under 500-600nm peaking at 540 nm and 543 for respectively Green Nanoparticles (NPs) and Green Nps in Fiber matrix.[75] This particular emission is attributed to the fact that Mn^{2+} takes place into tetrahedral Zn^{2+} sites. For, synthesized red nanoparticles, Emission Spectra can be obserfed under 254 nm. There is one characteristic peaking around 695 nm, characteristic of trivalent chromium ion occupying octahedral site , also several vibronic peaks are situated in close vicinity. [76]With fiber containing the red nanoparticles, this peak remains unaltered but with reduced intensity.
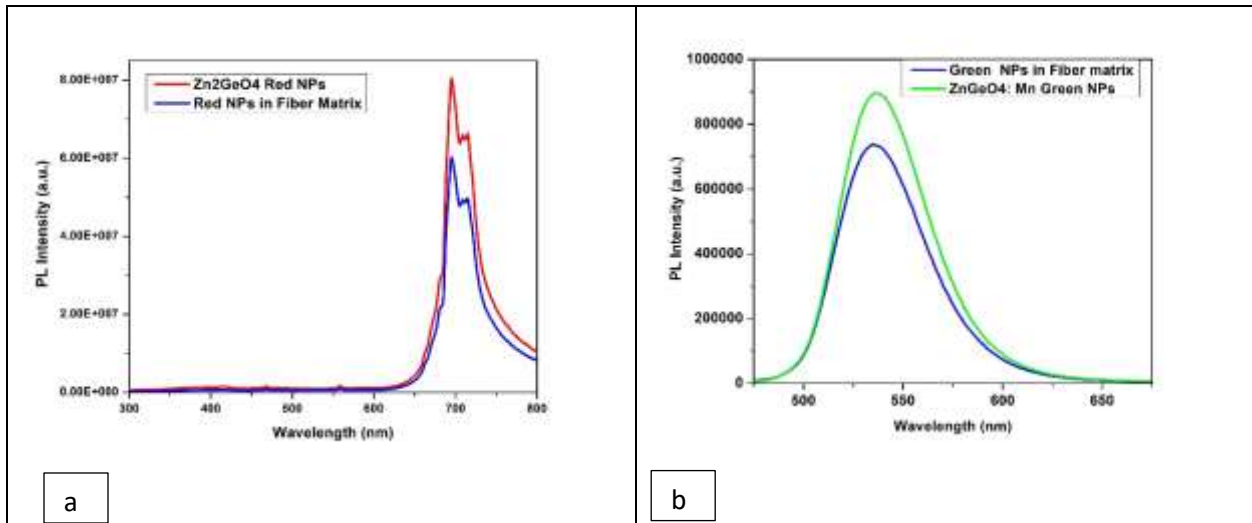
Fig 23: Comparison of Photoluminescence Emission Spectroscopy(PL) with a) Red

nanoparticles and b) Green nanoparticles

CHAPTER VI

CONCLUSION

Forcespinning^TM process was attributed to produce PU fibers. Three samples of different concentrations ranging from 15-17wt% and each having 4000,5000,6000,7000 rpms were made by forcespinning method and were used to analyze fiber morphology, production, thermal properties and wettability. All samples show very fine diameter in nanoscale range; the average fiber diameter is found to be from 0.23485±87.47 to 0.311113±90.26. respectively. For 16wt% concentration, measured fiber diameter remains most consistent for the 4000-7000 rpm range from 0.253315±93.97 to 0.268537±79.30. Among the different concentrations, PU 17wt% can be observed as the most productive. For 5000,6000 and 7000 rpm, process yields are respectively 28.87%, 31.6% and 32.95%. Thermal property analysis reveals that degradation occurs at 255-510C temperature range in a single step and the mass loss is very significant (92% mass loss).First DSCheating curve gives glass transition temperature or Tg as -48C and T_m as 160C. Water contact angle measurements revealed PU fibers as hydrophobic; for 14wt%,15wt%,16wt% and 17wt% PU sample contact angles are 107.49^o,113.17^o,113.77^o and 113.02^o respectively. Forcespinning^TM proves to be a great process candidate for continuous, homogenous and high amount of PU fiber production.

So, this facile method is recommended to engage it in further research and development of PU fibers and PU fiber composites with improved characteristics.   The biphasic method for synthetization of Mn doped Zn_2GeO_4 and Cr doped $ZnGa_2O_4$ were performed with trials to optimize their ingredients with retaining their luminescent under UV light , also a possible candidate to incorporate them in PU fibers. The synthesized particles are characterized with XRD test to verify and PL Spectroscopy test to observe their intensity of luminescence. The particles are attempted to integrate with direct Forcespinning, submerging the fiber mat in water-dmf-nanoparticle solution and scratching nanoparticles over fiber mat directly where the later one gave a better result. Further research on this area can assist to substantialize the loading of nanoparticles. The successful integration can be categorized   as a smart textile product capable of emitting luminescence out of cloths or other textile materials with useful applications

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