



IJRASET

International Journal For Research in
Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 10 **Issue:** VI **Month of publication:** June 2022

DOI: <https://doi.org/10.22214/ijraset.2022.44634>

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Micro and Nano Fiber Composite Coatings

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Abstract: Environmental friendly products are becoming popular and acceptable in industries due to the global limitation to the amount of volatile organic compounds (VOCs) released into the atmosphere. Low VOC compounds and technologies are also becoming a choice in the coatings and paint industry. Coatings can be made from water or solvent. In coatings from water, we use water as the solvent, therefore coating called water based coating and in the case of solvent-borne coatings, we used organic or inorganic compounds as solvents, therefore this coating called as solvent borne coating. Among all different types of solvents water is the greatest choice among these low VOC technologies for usage as a solvent to manufacture chemical compounds and Paints and coatings. because water is often recognized as a low-cost, safe, non-toxic, easily available and ecologically friendly solvent. Also nanomaterials is new field in research and development of material science. Materials can be one dimensional such as small particles, materials can be two dimensional such as fibres. Therefore in two-dimensional materials such as fibres (micro and nanofibers) use in many different applications such as medical, composites, aerospace, Building constructions etc. Nanofiber has the advantage of high surface area to volume ratio hence to decrease the coating defects. micro and nanofibers should be incorporated inside the coating matrix. This way one can improve the properties of water-based coatings. Hence low VOC solvent water with high surface area fibre is becoming a trend in composite coating and nanotechnology in fibres. This review provides information on Composite coatings, distinct fibres used in coatings and their applications, also effects of different aspect ratio of fibres on properties of coatings.

Keywords: Microfibers, Nano fibers, Polymeric fibers, Water-based Coatings, Composite Coating

I. INTRODUCTION

Polymers are the high molecular weight macromolecules that are formed from the low molecular weight small molecules by covalent bonds [1]. there are two types of polymers based on sources such as natural polymers and synthetic polymers. Natural polymers are those produced from plants such as wood, rubber, cotton, wool, leather, and silk, whereas synthetic polymers are manmade, can be produced in the laboratory such as polyethylene, polyamide, polyester, etc and this polymer is used for the production of useful plastics, rubbers, Coatings and fiber [2].

Coatings are the material that is formed from chemical substances such as Binders, volatile components, Pigments, and additives. Binders help to bind together with other substances in coating, Volatile components such as water or solvent helps to the formation of a film, Pigments are used for the aesthetic purpose by providing color to the coating and additives used to modify some properties of the coatings[3].Coatings can be made from water or solvent, in coatings from water, we use water as the solvent, and in the case of solvent-borne coatings, we used organic or inorganic compounds as solvents[4]. Because organic solvents are discharged into the atmosphere when solvent-borne paints are applied, the general public has an unfavourable perception of solvent-borne paints because of their toxicity and harmful to human beings. So in today's world more research is going on in water-based coating[5].

Nanotechnology is derived from the prefix "nano," which is derived from the Greek word for "dwarf," and nano, in technical terms, means 10⁻⁹ one-billionth of anything [6]. When the diameter of a fiber is changed from micrometer to nanometer dimensions, several properties change, including the ratio of surface area to volume, elasticity in surface functionalities, and highest mechanical properties (e.g., stiffness and tensile strength) compared to other substances. Nanofibers have the greatest ratio of surface-area-to-volume than microfibers [7].

II. COMPOSITE COATING

composite coatings are materials made up of two or more components that have been blended in such a way that they remain unique and identifiable [8]. Fig 1 indicates the ingredients of the composite coating. In key industries such as automotive, military, marine, and aerospace, polymer composites represent the most promising alternative to normally utilized materials, low weight fiber- composites (reinforcement can be done in a variety of ways) are particularly notable. Long threads, matting, and woven 2D or 3D textiles are examples). These materials have certain characteristics such as high specific strength [9].



Fig. 1 : Ingredients of the composite coating

Polymer nanocomposites provide improvement in various properties than virgin materials & hence used abundantly. Properties such as mechanical, thermal (stability and conductivity), ablation, electrical, optical, tribological, permeability, chemical resistance, and other areas [10]. the scientist did experiments to find the performance of composite coating on carbon Steel so that results show that coatings have a longer service life and better mechanical and surface qualities. Also, corrosion resistance, hardness, tribological, and thermal characteristics of steel are all improved by composite coating [11]. To examine the effects of chitosan and chitosan/MMT coatings on fresh-keeping, tangerine fruits were coated with chitosan and chitosan/MMT coatings. They add 1 percent of (w/w) MMT in composite coatings, the effects of maintaining nutritional content, reducing water loss, respiration rate, and cumulative degradation rate of fruits were more efficient and extended [12].

A. Classification of nanocomposite coatings

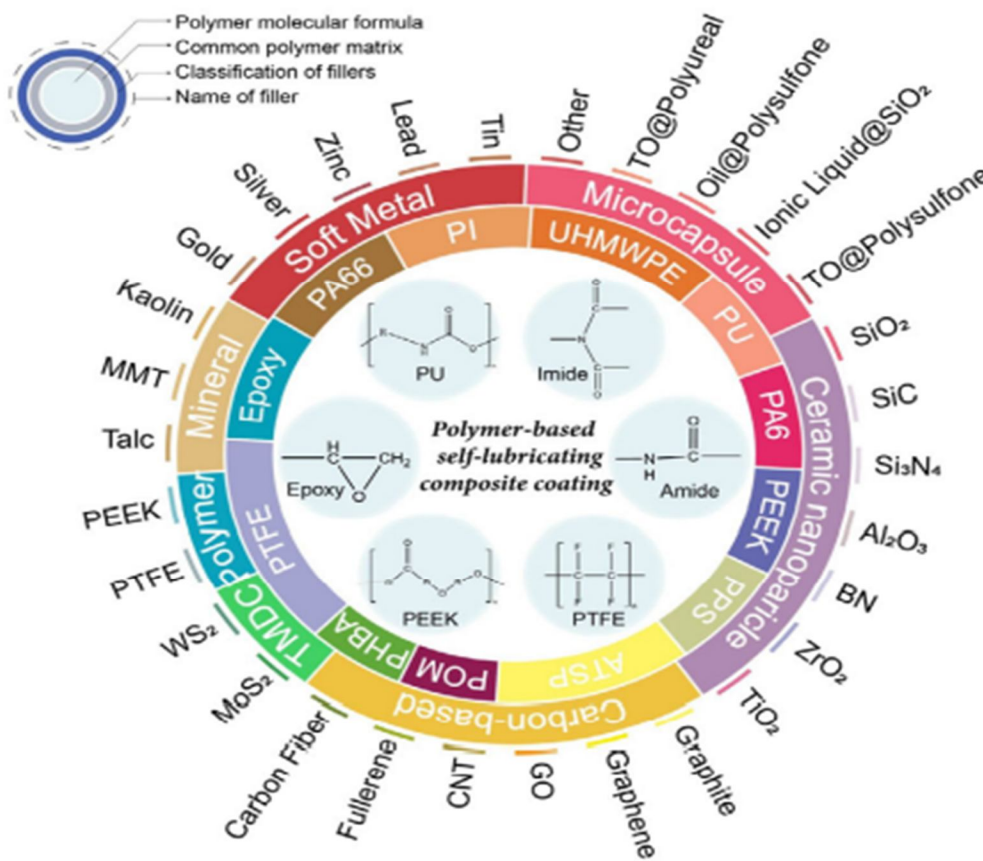


Fig. 2 : Matrices and fillers of composite coatings

Classification of composite coatings is based on several factors, including the Nano sized fillers used and the resin in which the filler nanostructures are disseminated [8]. Fig 2 indicates Matrices and fillers of composite coatings [13].

1) *Matrix / Resin*

Resins are polymeric materials that are used in coatings to make useful films after being coated. A high MW resin is required for effective film formation. Resins used in coatings are mostly two types thermoplastic resin and thermosetting resin. Thermoplastic resins are those resins that have low molecular weight and they need chemical reactions or curing agents to increase their molecular weight and to the formation of the film after application of coatings, and thermosetting resins are those resins that have very high molecular weight and that form uniform films without using a curing agent and no need of chemical reaction [14]. Fig. 3 indicates Resins/matrix used in composite Coatings.

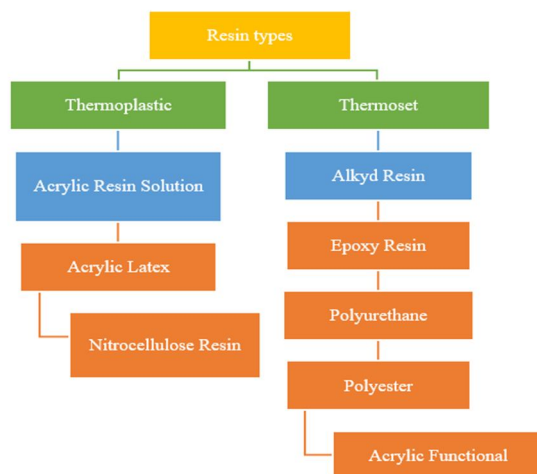


Fig. 3 : Resins/matrix used in composite coatings

2) *Nanostructured Fillers*

There are 3 types of nanostructured fillers used in nanocomposite coatings based on dimensions viz. 0-D, 1-D, 2-D, in which one-dimensional nanoparticles are the material that has one dimension, nanowires are the example of one-dimensional nanostructured fillers, and nanosheets are examples of two-dimensional nanostructured fillers [15]. Fig 4 indicates Types of Nanostructured fillers

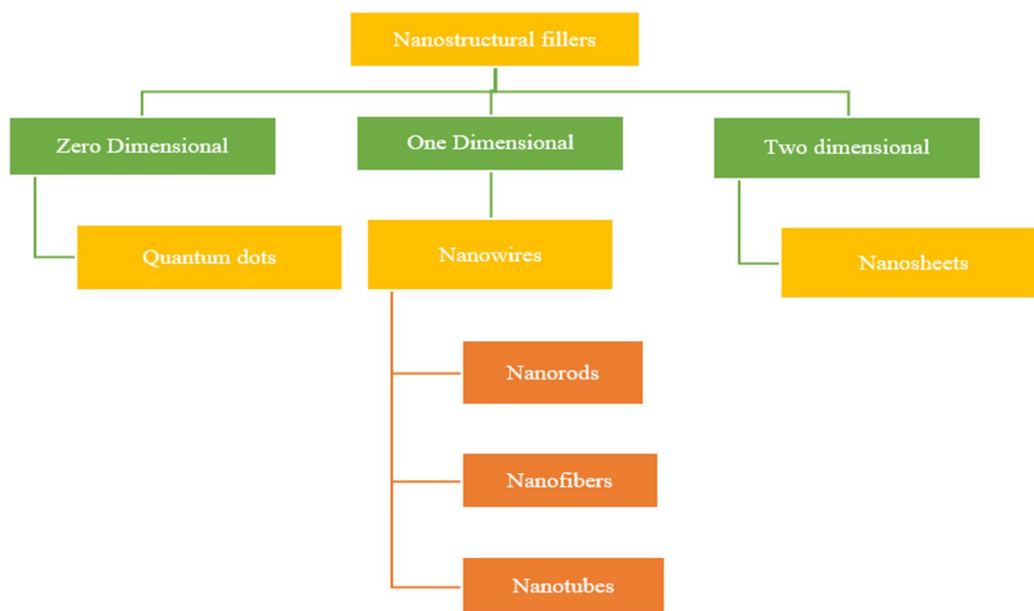


Fig. 4 : Types of Nanostructured fillers

Fillers used in coatings are given below-

Carbon Based- Graphite, Graphene, GO, CNT, Fullerene, Carbon Fibers

Ceramic Nanoparticles – SiO₂, Sic, Si₃N₄, Al₂O₃, BN, ZrO₂, TiO₂

Soft Metals – Gold, Silver, Zinc, Lead, Tin

3) *Carbon Based Fillers*

Carbon is Polymorphic and its forms are diamond graphite and Fullerene. Graphite, Graphene, GO, CNT, Fullerene, Carbon Fibers are some examples of carbon-based fillers.

Graphite is a great electrical and thermal conductor inside the layers but a poor conductor of electric and thermal properties perpendicular to the layers due to in-plane metallic bonding (because of the weak van der Waals forces between the layers). Because of its anisotropy, graphite may carry out chemical reactions by allowing the reactant (known as the intercalating) to reside between the graphene layers, resulting in the production of compounds (called intercalation compounds)[16].

Graphene has distinct properties compared to other materials such as high current density, ballistic transport, chemical inertness, high thermal conductivity, optical transmittance, and super hydrophobicity at the nanometre dimensions [17]. graphene exhibits exceptional strength and toughness With Young's modulus of 1 TPa and tensile strength of up to 100 GPa [13].

Fullerene is a graphene-based substance made up of huge carbon cage molecules that are thought to be a zero-dimensional (0D) benzene analog. Because of its spherical form, strong intramolecular nature, and poor intermolecular bonding, its lubricating action is of significant interest [13].

Carbon nanotubes (CNT) has one-dimensional carbon material with a ratio of diameter to height is more than 1000, that has superior physical and chemical characteristics compared to other carbon materials such as fullerene, graphite, and diamond, and also has exceptional electrical, thermal, and mechanical properties of carbon nanotubes using an excellent filler for lightweight composites of the polymer [18].

Carbon fibres a novel type of high-strength material, are commercially used as composite materials as reinforcements such as carbon-carbon composites, carbon fiber reinforced plastics, carbon fiber reinforced cement, carbon fiber reinforced polymers and. In all reinforcing fibres, fibers of carbon have the highest specific strength and specific modulus [19].

Ceramic Nanoparticles Because of their heat resistance and chemical inertness, ceramic nanoparticles are typically made up of carbides, nitrides, and oxides are mostly used in coatings. silica, Calcium phosphates, alumina, zirconium dioxide, and titanium dioxide are some of the materials used. good body response, High mechanical strength, pH and temperature resistance, high load capacity, high stability, absorption into hydrophilic and hydrophobic systems and several delivery routes such as oral, inhalation, etc. are all advantages [20].

Soft Metals Metallic nanoparticles such as gold, silver, palladium, and platinum have been widely employed due to their mechanical, chemical, and optical characteristics Among them, gold nanoparticles (GNPs) have antifungal and antibacterial properties, hence they're used in a variety of biomaterials and wide range of therapeutic uses in biosensors, medicines, and protein, gene, and medication delivery systems. They also increase the mechanical characteristics of materials, resulting in better results. They come in a variety of sizes and concentrations to demonstrate their therapeutic effects [21].

B. *Methods for Synthesis Composite Coatings*

A surface coating can increase the surface qualities while lowering the failure rate. Chemical vapor deposition, physical vapor deposition methods, laser cladding, laser melt injection electroplating composite, and electroless plating have all been used to protect component surfaces [22].

III. FIBRES

Fibre, derived from the Latin word fiber, is a natural or manufactured material that is much longer than its breadth. Fibers are often utilized in the manufacturing of other materials. Fibers are substance-like hair that comes in isolated elongated pieces or filaments like continuous.

They are capable of being spun into filaments, thread, or rope. They have the potential to be employed as a component of composite materials. They can also be matted into sheets and used as goods like paper or felt. Nanofibers can be synthesis from electrospinning methods such as solution electrospinning and melt electrospinning [23].

A. Classification of Fibers

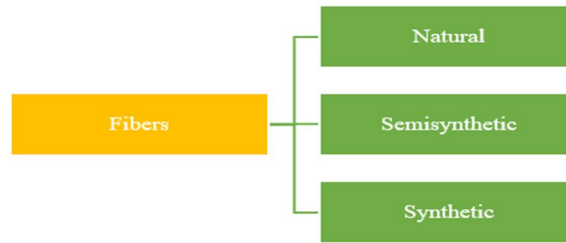


Fig. 5 : Classification of fibers.

Fibers come from sources such as from nature and from the laboratory, such as natural fiber, synthetic fibers, and semi-synthetic fiber which is a combination of synthetic and natural fibers. Fig 5 indicates the classification of fibers.

B. Natural Fibres

Natural fiber comes from various sources such as plants, animals. Natural fibers can be categorized based on where they came from. Fig. 6 indicates types of natural fibers

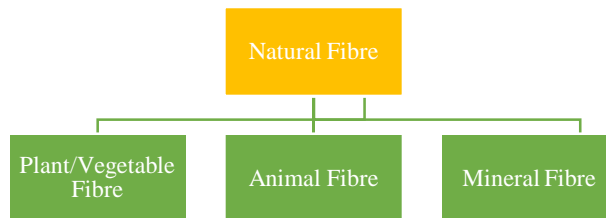


Fig. 6 : Types of natural fibers

Natural fiber composites provide several distinct properties. Because fibers have specific weight is low, it has a specific strength and stiffness is higher compared to glass fiber. It is a renewable resource. It can be produced with little investment and at a low cost, making it an appealing product for low-wage countries. Advantages of natural fibers are Tool wear is reduced, working conditions are healthier and there is no irritation skin [24].

Natural fibers are less abrasive preventing equipment damage. Natural fibers are less dense compared to mineral fibers resulting in lighter reinforcement with greater particular characteristics. This is of importance to the automotive and aerospace sectors which are always looking for methods to decrease vehicle weight. Furthermore, unlike mineral reinforcements such as glass fibers, natural fibers are safe to manipulate and are not hazardous to humans [25].

1) Plant / Vegetable fibre

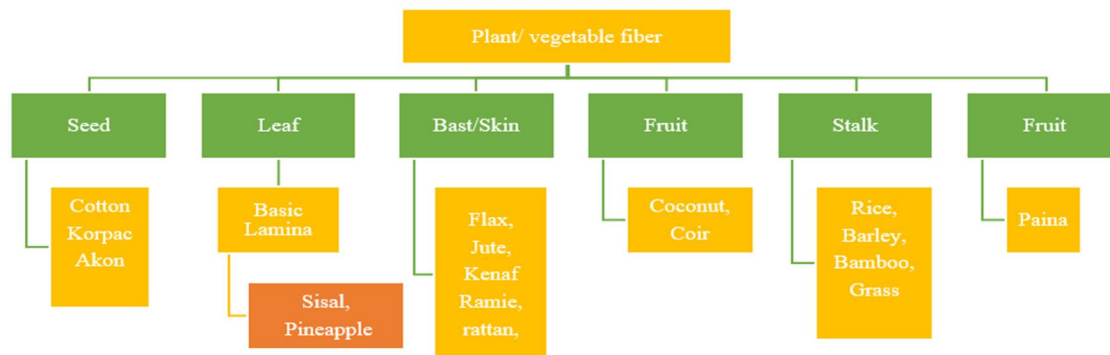


Fig. 7 : Plant and vegetable fibers

Vegetable fibers were tested with asbestos and synthetic fiber replacements. Fig. 7 indicates Plant and vegetable fibers, When materials are easily available natural vegetable fibers such as sisal, bamboo, fique, flax, jute, hemp, and ramie are utilized. Their use is motivated by the desire to save money on raw resources and contribute to the sector's long-term viability. Advantages of vegetable lignocellulose microfibers include Low real (1300-1500 kg/m³) and an apparent density (400-1500 kg/m³), high specific stiffness and strength, biodegradability, renewable character, low processing energy in the case of chopped natural fibers, and availability [26]. Fig. 7 indicates Plant and vegetable fibers

Table 1 -Types of Plant/vegetable fibers

Sr. No.	Type of Fiber	Plant origin	Diameter (μm)	Length (mm)	Aspect ratio (l/d)	References
1	Sisal	Leaf	18.3-23.7	1.8-3.1	115	[99],[100]
2	Ramie	Stem	28.1-35.0	60-250	4639	[99],[101], [102], [103],[104]
3	Pineapple	Leaf	20-80	-	-	[99],[105],[106], [107]
4	Kenaf	Stem	7.7-21.9	2.0-2.7	119	[99], [108],[109],[110]
5	Jute	Stem	15.9-20.7	1.9-3.2	157	[99],[111],[112],[113],[114], [115],[116]
6	Hemp	Stem	17.0-22.8	8.3-14.	1 549	[99], [117],[118],[119]
7	Flax	Stem	17.8-21.6	27.4-36.1	1258	[99], [119]
8	Cotton	Seed	11.5-17	20-64	2752	[99],[120],[116],
9	Coir	Fruit	16.2-19.5	0.9-1.2	64	[99],
10	Banana	Leaf	-	2-3.8	-	[99],[121],[122]
11	Abaca	Leaf	17.0-21.4	4.6-5.2	257	[99],[123],[124],[125]
12	Bamboo	Stem	10-40	2.7	-	[99],[126],[127],[128],[129]

2) *Animal fibers*

After plant fibers, fibers that come from animals are the second most important source of natural fiber for composite reinforcing. Examples of Animal fibers such as silk, wool, hair, and feathers. Wool fibers come from sheep, alpaca, angora, bison, cashmere, muskox, and other animals. There are numerous sources for each type of animal fiber such as silk, hair, and feathers [27]. fig. 8 indicates animal fibers

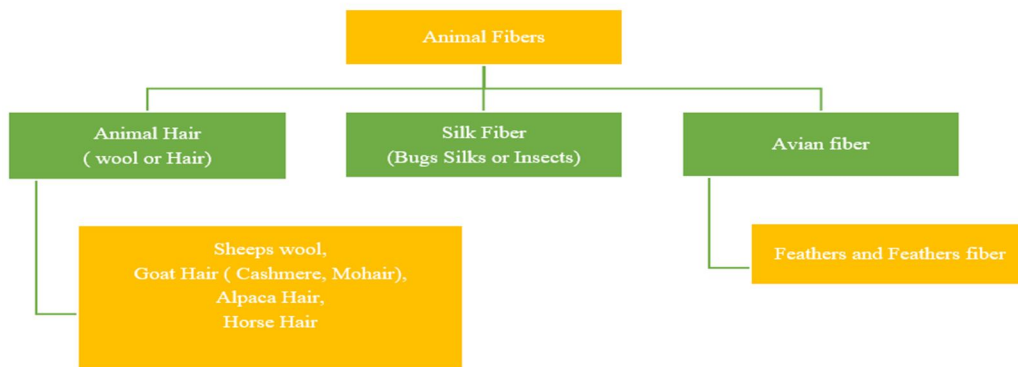


Fig. 8 : Animal fibers

- a) *Cashmere*: is a goat-derived animal fiber. This fiber is delicate and slender making it ideal for high-end apparel. Cashmere fiber, on the other hand, is 10 times more expensive than wool fiber due to its lower yield. As a result, in the business, producers typically combine cashmere with fine wool fiber in varying proportions to spin considering the economical front[28][29].
- b) *Silk*: is one of mankind's earliest fibers. Silk is an animal fiber generated by some insects for the construction of cocoons and webs. Silk is structured by repeated hydrophilic and hydrophobic peptide sequences and it is a high molecular weight organic polymer [30]. Silks are spun into fibers by some lepidopteran larvae, including silkworms, spiders, scorpions, termites, and flies [31].

c) *Wool*: has unusual physical and chemical qualities that make it very flexible due to its distinct wool compositions and macromolecule spatial structure, particularly in terms of molecular conformation [32]. Wool fibers may be used to make technological items like woolen fabric, felt, blankets, and cushion material. Furthermore, numerous beautiful fabrics made of wool, such as tapestries and wool carpets, provide individuals with a priceless and lovely feeling.

C. Synthetic Fibres

Fig 9 indicates Classification of Synthetic Fibers

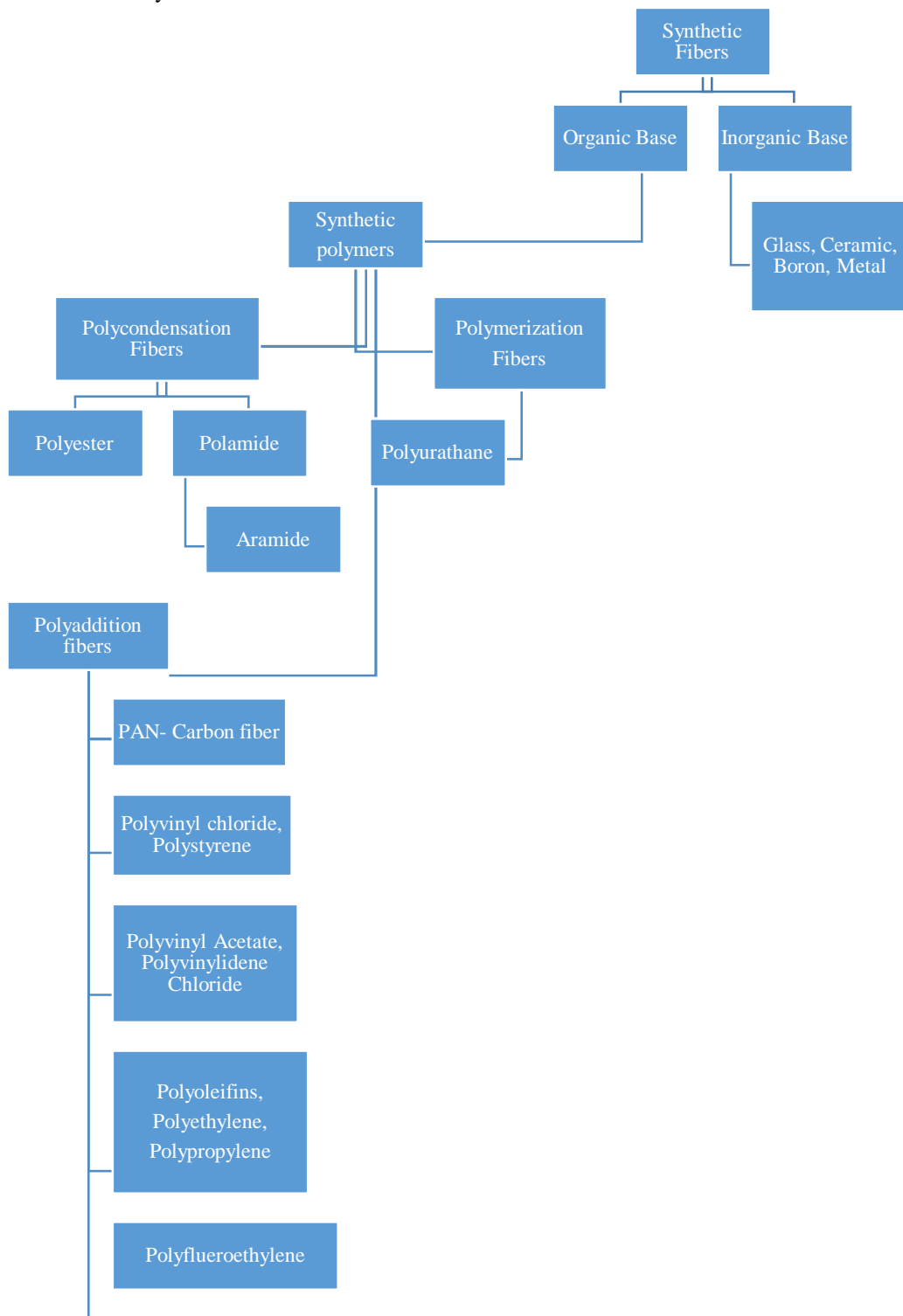


Fig 9 : Classification of Synthetic Fibers

1) Polyester Fibre

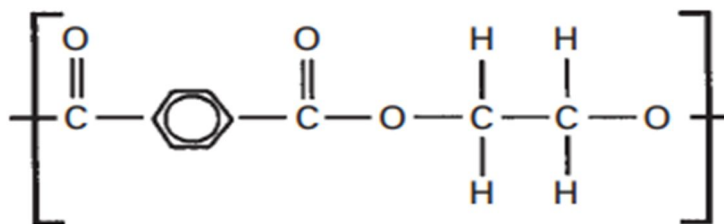


Fig. 10 : the structure of PET

Fig. 10 indicates the structure of PET [33]. Polyester fibers account for approximately 63.5 percent of global PET output.[34].The commercial methods of dimethyl terephthalate (DMT) and terephthalic acid (TPA) are used to make PET [35]. Poly (ethylene terephthalate) is a thermoplastic, semi-crystalline, and linear polymer that belongs to the polyester family. A chemical molecule is distinguished by its repeated ester groups.PET is typically made by a poly-condensation (step-growth) process at temperatures between 240 and 260 °C and pressures between 300 and 500 kPa, ethylene glycol (EG) combines with terephthalic acid, producing water[34].

Polyester fibers like nylon are produced by melting linear-condensation polymers and then drawing them. A stretch ratio of 5 is used in the drawing procedure, the same as in nylon. Polyester fiber is drawn at a temperature above its glass transition temperature of 80 °C [33]. Polyester fibers have good resilience, low moisture absorption, and dimensional stability, good weather and light resistance, great wear resistance, strong abrasion resistance, and good cotton blending ability. They are moderately flame resistant, microbe and insect resistant, physiologically inert, and thermoplastic [35]. PET fibers are rapidly being utilized in the textile sector for a variety of applications, like filtration[36],[37][38]. composites[39][40]. tissue engineering[41][42]. and electronic textiles.[43].

2) Polyamide Fibres

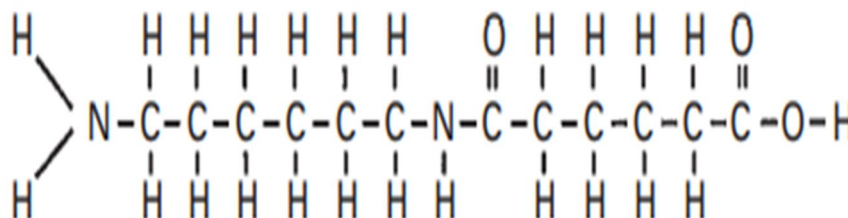


Fig.11 : structure of nylon

Fig.11 indicates the structure of nylon [33] Carothers at DuPont was the first to synthesis polyamide in the 1930s [44]. Nylon is a general term for a group of polymers known as polyamides [45]. It was one of the earliest synthetic polymers that were utilized in fiber applications.

Aromatic polyamides and aliphatic polyamides are two types of PAs. Aromatic PAs have aromatic rings in the main chain, whereas aliphatic PAs have solely aliphatic chains. Aliphatic PAs are typically made via condensation polymerization or ring-opening polymerization [46].

Polyamides are produced from odd diamines and even dicarboxylic acids that are aliphatic [47].Melt spinning and drawing procedures are used to make both nylon 6 and nylon 66 fibers [48]. The intermolecular interactions associated with hydrogen bonding between the polyamide links help Nylons produce excellent fibers [49]. Alkalis and most common organic solvents are not a problem for polyamide fibers [50]. Both fiber types have strong tenacity and impact strength equivalent wear and abrasion resistance, good resilience, and excellent fatigue behavior [51]. polyamide (PA6) is used in different industrial, apparel, and medical applications including wound sutures, artificial tendons, and medical packaging because of its excellent wear resistance, strength, toughness, good elastic recovery, , high resistance to rupture appearance retention, ease of coloration, and, low initial modulus [52].

3) Aramid Fibre

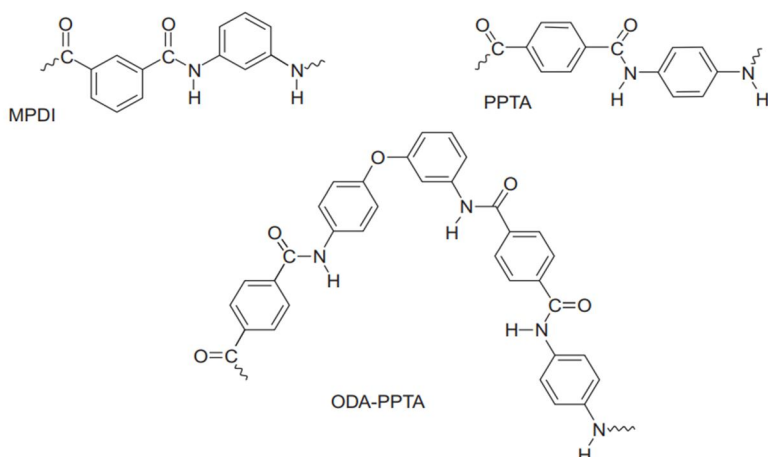


Fig.12 : structure of the Aramid Fibre

Fig. 12 indicates the structure of the Aramid [53]. Aramid fibers are also known as PPTA (polyphenylene terephthalamide) fibers [54]. Aramid fibers are high-performance fibers [55]. These types of fibers are aromatic with excellent heat resistance, fatigue resistance, chemical, corrosion resistance, and exceptional mechanical strengths. Kevlar fiber is manufactured of para-aramid and has extraordinary mechanical qualities; its modulus is over 120 GPa and tensile strength is at 3.6 GPa [56]. It can keep good strength, modulus, and high-temperature resistance because it has a high specific surface area and high aspect ratio [57]. It has been widely used in composite reinforcement[58][59][60]. electrical insulating materials[61][62]. adsorption and filtration media[63]. battery separators[64]. flexible electrodes[65]. and biological tissue[66].

4) Polyolefins fibers

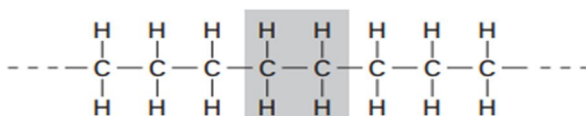


Fig. 13 : Structure of Polyethylene

Fig. 13 indicates the Structure of Polyethylene [33]. Polyethylene's simple chemical structure and controlled semi-crystalline shape make it a cost-effective and flexible material for a variety of applications such as composite armours, Vehicle chassis, prosthetic implants, and more fabrics[67]. Ultra-high molecular weight fibers have 95% crystalline because it is a highly ordered structure with almost all full chains are aligned[68]. Today, ultrahigh-molecular weight polyethylene (UHMWPE) fibers are commercially used with tensile modulus of 130 GPa and average tensile strengths of 3.7 GPa [69]. Gel-spun polyethylene fibres are high-modulus, ultra-strong fibers made from simple and flexible polyethylene molecules. High-strength, lightweight polyethylene fibres are what they're termed [70]. fibres from Polyethylene increase the impact strength, flexural strength, modulus of elasticity of composite materials[71]. ultra-high molecular weight polyethylene (UHMWPE) fibers have been widely utilized in ballistic armour and ropes Because of their low density, high strength, and excellent fatigue resistance [72]. ultra-high molecular weight polyethylene Fibres have a low density and excellent physical and mechanical qualities [73]. for the first time, "gel-electrospinning" is used to create microstructures of polyethylene with diameters smaller than one micron [74]. the modulus and tensile strength of ultrahigh-molecular-weight polyethylene (UHMWPE) fibres generated by a gel-spinning technique are impressive. The fibres are also very strong and chemically resistant[75]. high-density polyethylene, Low density, and medium density are the three primary classes of polyethylene, based on the molecular density and crystalline of the polyethylene structure [76]. PE is robust, abrasion-resistant, impact-resistant, and has a low water absorption rate, all at a reasonable cost [77]. fibre from Polypropylene (PP) is one of the lightest manmade fibres available, and it makes a bulk quantity of non-woven polyolefin fibres, which has tremendous economic importance due to their distinct characteristics. mechanical strength, hydrophobicity, and outstanding chemical resistance are some important qualities of PP fibres [78].

IV. APPLICATIONS OF NANOFIBERS

Fibres are used in various applications such as gas filtration [79]. controlled drug delivery[80]. in lithium-ion battery[81]. wastewater treatment[82]. Fuel Cell Electrolytes[83]. Dye Pollutant Degradation[84]. super capacitors [15]. triboelectric Nano generator[85]. micro gas sensor[86]. protective masks[87]. analytical chemistry[88]. Chemical Separation[89].

V. MICRO AND NANOFIBER COMPOSITE COATINGS

Composite coating technology was created to meet industrial needs for coatings with specifications that go beyond the capabilities of traditional coating technologies [90]. Composites are materials made up of two or more components that have been blended in such a way that they remain unique and identifiable [8]. Hardness, wear resistance, impact strength, corrosion resistance, tensile strength, and flexural strength are some of the mechanical qualities increased as we make composite coatings[91][92][93][94]. composite coatings are used in many applications such as tissue engineering[95]. Antibacterial purpose[96]. moulds, automobile parts, and general wear components.[97]. self-lubricating [98].

Table 2 Micro and Nano fibre composite coatings

Sr. No.	Fibre used	Type of coating	Results	Reference
1.	Tetra aniline based conducting Nanofiber (TANF)	waterborne epoxy coatings	<ol style="list-style-type: none"> 1. Block the pinholes and cracks present in the coating 2. remarkably improve the performance of corrosion protection by the formation of a passive layer of metal oxide 	[130]
2.	CNFs with high lignin content (LCNFs) and BEs	water-based acrylic coatings	<ol style="list-style-type: none"> 1. hardness level increases (2–3 times higher than virgin coating) 2. higher abrasive resistance 	[131]
3.	Polyamide (PA-6) Nano fibre	coatings on the aluminium surface	<ol style="list-style-type: none"> 1. decrease the corrosion currents and corrosion rate and also increase the corrosion resistance of a coating 2. increasing of high voltage for preparation to electro spun nanofibers lead to an increase in the corrosion resistance of the metal surface 	[132]
4	Super-hydrophobic polyvinylidene fluoride (PVDF)/fluorinated ethylene propylene (FEP)/carbon nanofibers (CNFs)		<ol style="list-style-type: none"> 1. improve the hydrophobicity of the formed coating by increasing the addition of FEP 2. behaves good wear-resistance can be increased because of water repellent coating 3. The adhesive ability of the formed coating by using fibres is superior compared to commercial coatings 4. excellent corrosion protection ability 5. The super hydrophobic coating has wear-resistance 5 times higher than the virgin PVDF coating and commercial fluorocarbon coating 	[133]
5	Carbon fibres	PTFE/CF	<ol style="list-style-type: none"> 1. Good friction and wear properties. 	[134]

		composite coatings	<ol style="list-style-type: none"> shows good hydrophobicity prevents the extensive destruction of composite coating Maintain wear mechanisms of PTFE/20% composite coatings. 	
6	Nylon 6/6, Poly (hexamethylene adipamide)		<ol style="list-style-type: none"> 60 % of microfibers can be controlled to be aligned within 60° to 90° of the azimuthal angle regardless of microfiber length. An increase in the microfiber length decreased the surface density of the fibers. 	[135]
7	Poly(vinyl) alcohol (PVA)/Nano silica (SiO ₂) based electro spun nanofibers		<ol style="list-style-type: none"> Improves the scratch-resistance tensile properties and of the surfaces. 	[136]
8	Poly(lactic-co-glycolic acid) (PLGA) nanofibers	poly(e-caprolactone) (PCL) film	<ol style="list-style-type: none"> delivery of combinatorial antimicrobial agents from various metallic implantable devices Effectively decrease bio film-associated infections in patients. 	[137]
9	Suffocated polyaniline (SPANI)	epoxy coatings on the steel substrate	<ol style="list-style-type: none"> Excellent protective performance with high impedance modulus. enhanced the anticorrosive property of composite coatings via forming a metal oxide film composed of Fe₂O₃ and Fe₃O₄ 	[138]
10	Electro spun PET nanofibers	LDPE film	<ol style="list-style-type: none"> the Nanofiber dispersed films show extraordinary good resistance to gas permeability improvement in mechanical, dart impact, and sealing properties 	[139]

VI. CONCLUSION

This paper give us the brief review about micro and Nano fibres used in coating such as natural fibres and synthetic fibres, also the review of composite coatings such as matrices used in coating and different fillers used in coating. Also we get information about which properties change as we add different polymeric micro and Nano fibres in coatings. As we convert the size of fibres from micro to Nano many properties are changed.

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