Functional Finishes of Acrylic Fibers Using Different Technologies

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Received: 12 November 2013; Revised: 14 December, 2013; Accepted: 20 December 2013.

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ABSTRACT

The current article aims to focus on conventional and the recent technologies used in functionalization of acrylic fibers. Different technologies such chemical, grafting, thermal, irradiation, plasma, biofinishing, microwave and nanotechnology have been highlighted in this review. The functional finishing properties imparted to acrylic fibers were flame retardation, ion-exchange, improved wettability and dyeability, antistatic resistance, UV-protection, thermal stability, carbonization and antibacterial resistance.

Key words: Functional finishing, acrylic fibers, chemical modifications, thermal, irradiation, plasma, bio-finishing, microwave, nanotechnology.

Introduction

Acrylic fiber in which the fiber-forming substance is any long chain synthetic polymer composed of at least 85% by weight of acrylonitrile units [-CH2-CH(CN)]. Acrylic fibers are produced by two basic methods of spinning (extrusion), dry and wet. In wet spinning, the spinning solution is extruded into a liquid coagulating bath to form filaments, which are drawn, dried, and processed [1]. Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with an average molecular weight of ~100,000, about 1900 monomer units. The Dupont Corporation created the first acrylic fibers in 1941, and trademarked them under the name “Orlon”. Acrylic has a warm and dry hand like wool. Its density is 1.17 g/cm³ as compared to 1.32 g/cm³ of wool. Acrylic has a moisture regain of 1.5-2.0% at 65% relative humidity (RH) and 25°C. It has a tenacity of 5 gm/denier in dry state and 4.8 gm/denier in wet state. Breaking elongation is 15% on (both states). It has a good thermal stability. Acrylic shrinks by about 1.5% when treated with boiling water for 30 min. It has a good resistance to mineral acids. The resistance to weak alkalis is good, while hot strong alkalis rapidly attack acrylic. It has an outstanding stability towards commonly bleaching agents [2, 3]. Acrylic fibers used as knit Jersey, Sweater, blankets, wrinkle resistant fabrics, pile and Fleece fabrics, carpets and rugs [1]. Various modifications of the acrylic fibers are targeted to attain better properties.

Functional finishing with traditional methods:

Various chemical modifications are used to impart certain desired properties to acrylic fibers. It was carried out to improve dyeability, hydrophilicity, conductivity, antimicrobial, fire resistance, tensile strength, and performance properties (smoother surface and anttipilling properties). Antimicrobial acrylic fibers:

Antimicrobial property is generally important for textiles. The bactericidal textiles prepared are lethal not only to pathogenic bacteria but to fungi as well [4, 5]. The polyurethane prepolymer was extended with chitosan of two different molecular weight used as finishing agent for acrylic fabrics. Pretreatment of acrylic fabrics with hydrazine hydrate was found to improve the uptake of the polymer by the fabric. The antibacterial activity of the acrylic fabric treated with the polyurethane-chitosan solution was improved even after 15 washing times [6]. Acrylic fabrics are treated with different concentrations of chitosan and chitosan/copper sulphate. The treatment with chitosan/copper sulphate gave the highest antimicrobial activity than treatment with chitosan only [7]. The antibacterial fibers were prepared by heat-treating acrylic fibers containing antibacterial metallic compounds at pH 1–6 [8, 9].

The antimicrobial cationic dyes were employed in dyeing acrylic fabrics. It was found that these functional dyes could be effectively introduced to acrylic fibers to achieve simultaneous coloration and functional finishing effects. All the dyed fabrics exhibited antimicrobial efficacy against Escherichia coli and Staphylococcus aureus. The washing durability of antimicrobial functions on the treated fabrics was further studied [10]. The fabrics with silver content 0.5–100 ppm, useful for towels, handkerchiefs, and sheets, contain
20-80% hydrophobic fibers, 80-20% hydrophilic fibers, and N-C\textsubscript{2}H\textsubscript{3}-aclylamino acid silver salts. Thus, acrylonitrile-methacrylate-sodium methallylsulfonate copolymer fiber was immersed in an aqueous solution of silver N-stearyl-L-glutamic acid, dried, spun with cotton, dyed, and woven into a pile fabric showing good water absorption and antibacterial activity against Escherichia Coli [11]. Silver-loading polyacrylonitrile hollow fiber was spun via the dry jet-wet spinning technique from a dope containing 0.5% silver nitrate. After flushing with water for 60 days, the silver content in the hollow fibers decreased to 0.1%, and still showing antibacterial activity against Escherichia coli and Staphylococcus aureus. On the other hand, by permeating water through the hollow fibers, silver content was decreased faster and may require periodical replenish [12]. The acrylic fibers containing silver and/or zinc exchanged titanium silicate particles that act as slow-release antibacterial agents. The antibacterial agents is insoluble water, detergent, organic solvents and is thermally stable, so its activity is permanent [11, 13].

Ionic interactions can be used in antimicrobial finishing of acrylic fabrics with quaternary ammonium salts. The adsorption of cetylpyridinium chloride (CPC) on acrylics is higher and quicker than that of benzyl dimethyl hexadedyl ammonium chloride (BDHAC), possibly due to the size difference. Varying finishing pH conditions in a slightly acidic range and addition of sodium sulfate appear to be less important in affecting uptakes of the salts [14]. Polyacrylonitrile-co-3-allyl-5,5-dimethylhydantoin (Cop7-1) was prepared by a free radical polymerization process. The copolymer was blended with polyacrylonitrile (PAN) in a NaSCN aqueous solution, and the mixture was employed as a spinning solution. The blend fibers showed good antibacterial ability [15].

The antimicrobial functions assigned to acetyl pyridine chloride embedded on fabrics and their durability formed through ionic bonds among the anionic groups on fiber and cationic acetyl pyridine chloride, which depend on the quantity of the agent embedded during the finishing treatment. The aggressive alkaline conditions of the treatment may cause negative impacts both on mechanical properties and chromaticity of the textile material, due to a potential alkaline reaction induced by the acrylic polymers, resulting in C=N conjugated systems [16, 17].

### UV-protection:

Titanium dioxide is widely used UV blocking of acrylic fibers. Titanium dioxide is a photocatalyst; once it is illuminated by light with energy higher than its band gaps, the electrons in TiO\textsubscript{2} will jump from the valence band to the conduction band, the electron (e\textsuperscript{-}) and electric whole (h\textsuperscript{+}) pairs will form on the surface of the photocatalyst. The negative electrons and oxygen will combine into O\textsubscript{2}\textsuperscript{2-}; the positive electric holes and water will generate hydroxyl radicals. Since both are unstable chemical substances, when the organic compound falls on the surface of the photocatalyst, it will combine with O\textsubscript{2}\textsuperscript{2-} and OH\textsuperscript{-} respectively and turn into carbon dioxide (CO\textsubscript{2}) and water (H\textsubscript{2}O) [18].

### Fire-resistance acrylic fibers:

Acrylic fibers were treated with sodium hydroxide at 90°C, washed and then treated with an aqueous calcium hydroxide solution to give modified acrylic fibers. Poly(ethylene terephthalate) staple fibers with a degree of holowness (35 %) were sprayed coated with a composition mainly containing di-Me polysiloxane and heated to give coated fibers. A carded web comprising 70 % of the above coated fibers and 30 % modified acrylic fibers was made into nonwoven fire resistance fabric that can be used for bending, stuffing and bed pads. The staple fibers containing synthetic fibers, heat-bondable and modified acrylic fibers or fibers having a crosslinked structure with carboxyl groups in the form of metal salts were coated with silicones [19, 20].

The fibers were manufactured by treating a sample of saturated acrylic fibre, with intermediate rinsing steps, in an autoclave with: (1) a hydrazine solution at 100°C-120°C preferably at 105°C for crosslinking, (2) a sodium hydroxide solution for hydrolysis, (3) a neutralization solution such as sulphuric acid, and (4) a salt solution of, e.g., zinc acetate. The treated fibers have a denier with at least 1.5 times, preferably 1.8-2.6 times that of the untreated fibers, a tenacity of >15 cN/tex and an elongation about 30%, this fibers has fire resistant property [21].

The polyacrylonitrile (PAN) fibers was treated with metal acetate ((M (II) CH\textsubscript{3}COO)\textsubscript{2}, M(II) \textsuperscript{2+} =Cu(II), Zn(II), Mn(II) and Ni(II) to improve flammability. Thermal properties of the modified polyacrylonitrile (PAN) fibers were studied by DTA, TG, GC and cone calorimetry. The apparent activation energies for the decomposition of the unmodified and modified PAN fibers were determined using Kissinger equation and Broido equation [22].

### Thermal treatment:

PAN fibers were stabilized in a continuous oxidizing furnace with 3.4 m/min speed in air. The oxidized PAN fibers of different colours were cut down as testing samples. The oxidized PAN fibers were mounted on a scanning electron microscope (SEM) holder, and their cross-sections were etched using dimethyl sulphoxide (DMSO) at room temperature for 2 min. The results, the cyclization propagation path involves four steps: (i) cyclization in the amorphous region on the surface of the fiber,
(ii) cyclization in the amorphous region in the center of the fiber, (iii) cyclization in the crystal region on the surface of the fiber and (iv) cyclization in the crystal region in the center of the fiber. The aromatization index (AI) value was calculated from AI = Ia/ (Ip + Ia) 1448 where Ia is the diffraction intensity of the aromatic structure at 20 -26°C and Ip is the diffraction intensity of the PAN crystal at 20 -17°C. Aromatization Index (AI) = Ia/ (Ip + Ia) [23].

PAN fabrics are treated with chemical/thermal treatments (potassium dichromate or hydroxylamine then heat treated in air) under various conditions. Thermal treatment of PAN fabrics in air led to an increase in the tensile strength as compared to the untreated one, accompanied by a decrease in the elongation property. The results of both dichromate/thermally and hydroxylamine/thermally treated PAN fabrics showed an increase in the tensile strength than the untreated fabric, but the elongation has decreased. All treatments gave some changes in infrared spectra, these show some decrease in the nitrile group. It was found that the AI increased with increasing the temperature and with hydroxylamine/thermal treatment. The hydroxylamine/thermal treatment led to a decrease in melting temperature than untreated one [24].

According to the distribution coefficients the order of decreasing selectivity of the cation exchanger for the various metal ions was Cu²⁺ > Zn²⁺ > Cr³⁺ > Hg²⁺ > Cd²⁺ > Pb²⁺ > Ni²⁺ > Co²⁺. The product could be reused after regeneration with diluted nitric acid. A modified synthesis method has been developed. A modified synthesis method has been developed. The carboxyl group containing hydrazine modified polyacrylonitrile fiber is an amphoteric ion exchange. The kinetics of the modified PAN fiber metal ions interaction have been found to be sufficiently rapid in most cases for the extraction of trace metals. The application of the new fiber for the construction of moving belt ion exchangers would offer some advantages. Channelling of ions cannot occur due to the structural properties, because no bead is needed, bead-related problems cannot occur [25].

The competitive binding of ions Cu²⁺, Pb²⁺, Cd²⁺, Ni²⁺, Zn²⁺ on the ion-exchange resins and chelate ion-exchange fibrous material Akvalit-2 has been investigated. Selectivity rows were obtained for examined samples. Competitive binding constants as well as rate constant of adsorption were calculated. Akvalit-2 was established to have the best sorption kinetics and affinity to Pb²⁺ and Cd²⁺ ions in comparison with conventional ion-exchange materials. Material TP207 showed a high affinity to Cu²⁺ ions [26]. Many methods (such as adsorption, electrophotolysis, ion exchange, membrane separation, precipitation, and so forth) are being used to remove the ions of the metals such as chromium, copper, iron, lead, silver, and zinc, from aqueous effluents [27, 28].

Polyacrylonitrile fibers were chemically modified by conversion of their nitrile groups into other effective adsorbent groups under a two-step process. At first, the modification process was initiated through hydrolysis of the fibers in an alkaline solution. In the next step, functionalization of the fibers was carried forward by thiourea. The modified polymer-metal complexes were obtained in aqueous solutions at different pH media of 2 to 8. The adsorption capacities of the samples towards Cr⁶⁺, Hg²⁺ and Pb²⁺ were in the given order of 0.73, 0.09, and 0.14 mmol/g (at pH 4). These results may be considered as an indication of higher selectivity of the modified fibers towards Cr⁶⁺ ions compared to Hg²⁺ and Pb²⁺ ions. The study on these modified ion exchange fibers (HTPANFs) for industrial effluents revealed that the maximum capacities of the modified PAN fibers towards Cr⁶⁺, Hg²⁺ and Pb²⁺ are 0.41, 0.05, and 0.11 mmol/g (at pH 4), in the given order. The thermogravimetric data indicated that the initial thermal stability of the modified fibers is lower than those of raw fibers due to conversion of nitrile groups into amine and thioamide functionalities [29].

**Functional finishing by grafting:**

Methyl methacrylate (MMA) was grafted onto commercial acrylic fibers (PAN) using azobis (isobutyro)-nitrile (AIBN) as an initiator. The optimum conditions for this grafting reaction were obtained with an MMA concentration of 0.7 M, an AIBN concentration of 0.0073 M, a reaction temperature of T 5 85°C and with a 60 min reaction time. Grafting yield, have occurred in fibers samples up to 13.5%. Grafting also slightly affected the fiber morphology. Grafting of poly MMA improved water absorption. The maximum grafting yield was 94% [30].

Polyacrylonitrile (PAN) fiber was grafted with casein after alkaline hydrolysis and chlorination reactions of the original fiber. Moisture absorption, specific electric resistance, water retention value, and mechanical properties were enhanced. The grafted PAN fiber has better hygroscopicity compared with the untreated one. With proper tensile strength, the modified fiber could still meet the requirement for wearing. A mechanism was proposed to explain the deposit of casein on the synthetic acrylic fiber, Figure 1. Casein-grafted acrylic fiber exhibits better hygroscopicity, anti-static property and spinnability, which gives the proof that the surface properties of the original acrylic fiber have been improved [31, 32].

A novel method of modifying polyacrylonitrile (PAN) fibers grafted with soybean protein (SP). The reactant of PAN-g-SP fiber was prepared based on chlorination of the hydrolyzed PAN fiber. The
grafting efficiency first increases with the increase of the addition of thionyl chloride (SOCl₂), chlorination time and temperature and then levels off. In grafting reaction, grafting efficiency increases at first and then declines significantly with increasing addition of sodium hydroxide (NaOH), grafting temperature and time. PAN-g-SP also exhibits good hygroscopicity and proper mechanical properties [33].

As one of the major techniques developed to achieve surface modification of polymeric materials, UV-induced surface graft polymerization has been widely applied as a simple, useful and versatile approach to improve the surface properties of polymers. UV-induced surface graft polymerization carried with (1) various initiating methods, controlled/living grafting, self-initiated grafting (grafting without the addition of photo initiators), graft polymerizations with monomer pairs able to form charge transfer (CT) complexes, grafting in liquid, vapor and bulk phase, and the substrates used for grafting; (2) the topography of grafted surface layers, including granular structure, crosslinked structure, and well-defined structure; and (3) the application of techniques to prepare functionalized polymer surfaces with designed performances, e.g., to obtain polymer materials suitable for biomedical applications, membranes or microfluidics % [34].

Recent Technologies in Functionalization acrylic:

Carbonization:

Some commercial PAN precursor fibers displayed double separated peaks and these fibers were of high quality because of their process stability during their conversion to carbon fibers of high performance. Some fabrication processes, such as spinning, drawing, could not apparently change the DSC features of a PAN precursor fibre. It was concluded that the thermal properties of a PAN precursor fiber was mainly determined from its comonomer content type and compositions [35].

Acrylic fabric wastes were reused to produce an activated carbon fabric. The precursor fabric was stabilized in the condition of as obtained at 250°C for 5 h to get the degree of stabilization of 79%. The stabilized fabric was subsequently carbonized with stepwise sequential heat treatment, denoted as the sequential multistage carbonization technique, followed by activation with steam. The specific surface area and the total pore volume changed little through stabilization and sequential multistage carbonization while the total weight loss increased almost linearly with the increase of heat treatment temperature. When the carbonized fabric was activated at 900°C for 5 min, both the specific surface area and the total pore volume increased abruptly to 2400 m/g and 31.15 cm³/g, respectively [36]. The observed changes suggest a change in the mechanism of activation from one involving principally gasification of amorphous or more reactive carbon at low burn-off to one involving principally attack of individual crystallites and their re-organization at higher burn-off [37].

To find out the high quality polyacrylonitrile (PAN) fibers, some differences are sought by comparison domestic PAN fibers with the foreign ones are used. The high-quality PAN fiber have high density, lower titer, higher or adequate tension strength, and they also have better conglomeration structure, smaller crystal dimension with dispersive distribution, less microvoids and flaws [38]. Carbon fibers are a significant volume fraction of modern structural airframes. Embedded into polymer matrices, they provide significant strength and stiffness gains by unit weight compared with competing structural materials. Our data highlight the predominance of the in-plane graphene properties in all graphitic structures examined [39]. The proper pre-oxidation time, pre-oxidation temperature, and pre-oxidation stretching ratio are the base of preparing high-quality CF. During pre-carbonization, the enhancement of the pre-carbonization temperature and the application of the pre-carbonization stretching are helpful to increase the tensile strength of CF, but the stretching ratio should
be controlled carefully by on-line tension values. The tensile strength of carbon fibers CF increases quickly below 1200°C and then slowly above 1200°C as the carbonization temperature raises. Even though during carbonization, a proper relaxation should also be explored in order to prepare optimal CF [40].

PAN-based 3000 filament batch and the shrinkage of PAN fibers were monitored by the displacement of weight. Stabilization was carried out between the temperatures of 180°C – 220°C, air flow of 0.3 m³/hr. The carbonization furnace was heated in high-purity nitrogen from room temperature to 1000°C at a rate of 5°C/min, and heating ceased when the temperature was reached. During stabilization in air, moisture acts as a plasticizer to reduce the Van de van force between molecular chains. Figures 2 and 3 show carbon fibers structure prepared from acrylic fibers [41].

Fig. 2: Carbon fibers structure.

Fig. 3: Carbon fibers structure.

Polyacrylonitrile (PAN) polymers are used as precursors for carbon fibers production. The obtained results showed that the addition of itaconic acid and methyl acrylate MA as co-monomers resulted a lower heat flow during the process comparing to the PAN homo-polymer. The cyclization temperature decreases when MA is incorporated into the terpolymer compared to the MMA terpolymer and increases when MAA is the acidic monomer. The acid co-monomer plays an important role in the
thermal behavior of the terpolymer. Among terpolymers, the one that acrylic acid (AA) is incorporated into the polymer (AN/MA/AA), exhibited one of the best thermal properties compared to other terpolymers: low cyclization temperature together with low heat effect. The itaconic acid, which incorporated into the terpolymer decreases the heat effect of the PAN terpolymer and the initial and peak temperatures, leading to a formation of carbon fiber with better mechanical properties [42].

Modification of polyacrylonitrile (PAN) fibers with cobaltous chloride has increased crystal size, crystallinity, and density, and also improved tensile strength and modulus of the resulting carbon fibers. The modification process improved the tensile strength, the tensile modulus as well as electrical conductivity by about 15% of the resulting carbon fibers at carbonization temperature of 1300°C. A higher stacking size (La), or a greater carbon basal plane in crystalline, is one of the reasons to improve the modulus and conductivity of the final carbon fibers [43]. The surface chemistry of porous carbons could be modified by various methods, such as, acid treatment, oxidization, ammonization, plasma, microwave treatment, and i.e. [44].

Functional finishing with gamma irradiation:

Gamma irradiation was used by many workers to improve some properties of acrylic fibers. The effect of irradiation dose on the dye affinity of acrylic fabric was monitored. Irradiated acrylic fabric showed a higher dye affinity for the used dyes compared to the un-irradiated fabrics. Fabrics irradiated to a radiation dose of 1 Mrad showed the highest dye affinity with high leveling of dyeing. The pH of the dyeing bath at which the highest color strength obtained was 3. A mechanism was proposed for the dyeing of acrylic fabrics with direct dyes in the presence of copper ions, Figure 4 [45].

![Image](image-url)

**Fig. 4:** Proposed mechanism of effect of gamma irradiation on dyeing of acrylic fiber.

Acrylic fibers containing alumina-zinc silicate were irradiated by electron beams at doses of 3-24 kGy. This study showed that the fibers irradiated attained greater antibacterial activity than non-irradiated fibers and also clarified the optimum irradiation dose range for fiber products [46].

Functional finishing with plasma technology:

Plasma treatment, as a clean, dry and environmental friendly physical technique, opens up a new possibility in this field. Plasma usually induce the following processes: dehydrogenation and consequent unsaturated bond formation, rapped stable free radicals formation, generation of polar groups through post-plasma reaction, and generation of increased surface roughness through referential amorphous structure ablation processes. In fact, plasma treatments allow modification of the textile surface behavior with a flexible process, which can impart particular properties to the fabrics, such as waterproofing, oil repellence, antistatic behavior, etc. In addition, plasma processes are characterized by the very small quantity of chemicals involved and by the absence of solvent or water, which are usually employed in traditional finishing processes. Figure 5 shows the Atmospheric plasma unit at North Carolina State College of Textiles [47].

The effect of different plasma treatments on the properties of acrylic fabrics for outdoor applications was explored. In particular, the possibility of substituting plasma processes for the traditional cleaning and waterproofing processes of outdoor acrylic fabrics was evaluated. The properties of the plasma treated acrylic fabrics have been compared with the characteristics of the fabrics traditionally treated. The resistance of plasma treatments to wear, UV and weather exposure has been also evaluated. Figure 6 shows plasma processes [48].

Acrylic fibers are treated by nitrogen glow-discharge plasma to promote surface antistatic properties. The treated surfaces are characterized by scanning electron microscopy (SEM), specific surface area analysis (BET) and X-ray photoelectron spectroscopy (XPS). Plasma treatment is found to increase the surface roughness, to modify the nature and density of surface functionalities, and to...
drastically improve the wettability and antistatic ability of acrylic fibers [49].

Usually three different types of plasma processes are referred to: One is the modification of surface structure of the material itself under the influence of the glow discharge mostly performed with non polymer is precursors such as noble gases, nitrogen, oxygen, hydrogen, ammonia or water vapor. The second is plasma polymerization i.e. the deposition of thin polymer film on the surface by using organic, organ silicone or organ metallic vapors. The third is the plasma grafting after activation of the surface by means of plasma treatment [50]. Acrylic fabrics were treated in low temperature plasma to increase the hydrophilicity to increase soil resistance, and improve dyeability. Three different modifications were applied. Fabrics were directly treated in acrylic acid, water, and argon plasma. Wettability, soil resistance, and dyeability of Polyacrylonitrile fabrics were significantly improved by these methods and more hydrophilic surfaces were created [51, 52].

![Image of atmospheric plasma unit at NC State College of Textiles]

**Fig. 5:** Atmospheric plasma unit at NC State College of Textiles.

![Image of plasma processes]

**Fig. 6:** Plasma processes.

Acrylic fabrics were processed with atmospheric pressure plasma generator and afterwards a fluorocarbon finish was applied through a traditional pad-dry-cure method. Two gas mixtures were tested (helium and helium/oxygen) with different plasma treatment times. The ageing of the finishing was simulated through repeated accelerated laundry cycles. The water and oil repellencies were measured through standard test methods. While the initial water and oil repellency did not change, the plasma treatment improved the durability of the finish after artificial ageing [53].

**Biofinishing:**

The surface of fibers has been modified by enzyme treatment. The newly formed amide groups were then able to react with the acid dyes typically used to stain natural fibers, conferring the coloring properties to the otherwise inert polymer surface [54]. Nitrile groups on the surface of acrylic fibers were selectively hydrolyzed to the corresponding amidic groups by nitrile hydratase from Arthrobacter. The dyeability with acid dyes on the enzymatically modified acrylic fiber was enhanced [55]. Hydrolysis of nitrile groups of acrylic fibers with enzymes from R. rhodochrous was studied. Surficial nitrile groups of acrylic fiber were hydrolyzed by the enzyme preparation to a maximum of only 16%. The dyeing efficiency was increased by enzyme treatment for both acid and cationic dyestuffs [56].

The enzyme used was a nitrile hydratase, a member of the class of nitrile converting enzymes. The pendant nitrile groups were selectively converted into the corresponding amides as assessed by x-ray photoelectron spectroscopic analysis. The
modified acrylic fibers became more hydrophilic [57, 58]. The major advantages of enzymes in polymer modification compared with chemical methods are milder reaction conditions and highly specific nondestructive transformations targeted to surfaces. Polyacrylonitrile Using X-ray photoelectron spectroscopy, enzyme preparations from Rhodococcus rhodochrous [56], Brevibacterium imperiale and Corynebacterium nitrophilus were shown to hydrolyze PAN. Interestingly, nitrile groups of granular PANs were converted into the corresponding acids by the sequential action of nitrile hydratase and amidase from R. rhodochrous, while 16% of surface nitrile groups of PAN fibers were converted to the corresponding amides by the nitrile hydratase. Owing to the enzymatic modification, the acrylic fibers became more hydrophilic and the adsorption of dyes was enhanced [54].

The hydrolysis of nitrile groups to carboxylic groups is the most common pathway for the microbial degradation of nitrile compounds. This reaction can proceed through two distinct pathways: the direct conversion catalyzed by nitrilase (EC 3.5.5.1) and the two-step conversion catalyzed by nitrile hydratase (EC 4.2.1.84) and amidase (EC 3.5.1.4). The nitrilase action on the acrylic fabric was improved by the combined addition of 1 M sorbitol and 4% N,N-dimethylacetamide. The color levels for samples treated with nitrilase increased 156% compared to the control samples. When the additives were introduced in the treatment media, the color levels increased 199%. The enzymatic conversion of nitrile groups into the corresponding carboxylic groups, on the fiber surface, was followed by the release of ammonia and polyacrylic acid. The application of the nitrilase for the acrylic treatment is intimately dependent on reaction media parameters, such as time, enzyme activity and formulation [59]. Review attempts to describe in detail the three major classes of nitrile-converting enzymes, namely nitrilases, nitrile hydratases and amidases. Various aspects of these enzymes including their occurrence, mechanism of action, characteristics and applicability in different sectors have been elaborately elucidated [60].

**Functional finishing with Microwave irradiation:**

Microwave dyeing was carried out under a variety of conditions in terms of the power and time of a microwave. The dyeability of acrylic fibers was significantly improved under microwave irradiation caused by the increased adsorption of the dye into fibers due to the local overheating and an amplified reaction probability between the dye and fiber. Dye adsorption at low concentrations using the microwave-based procedure is higher and much faster than conventional methods, but K/S is the same around the saturation point. The surfaces of microwave-irradiated acrylic fibers are rougher than conventionally dyed fibers, allowing the dye molecules to permeate and adsorb into the acrylic fibers. A power of 720 W and microwave irradiation time of 14 minutes have been found to be an optimum dying condition for acrylic fibers, although 5 minutes using 720 W microwave irradiation is enough to obtain the same dyeability as conventional methods [61].

**Functional finishing with nanotechnology:**

Nanotechnology is defined as the utilization of structures with at least one dimension of nanometer size for the construction of materials, devices or systems with novel or significantly improved properties due to their nano-size. Nanotechnology can be described as activities at the level of atoms and molecules that have applications in the real world. Nano-particles commonly used in commercial products are in the range of 1 to 100 nm. Nanotechnology also has real commercial potential for the textile industry.

Nanotechnology can provide high durability for fabrics, because nano-particles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function. In addition, a coating of nano-particles on fabrics will not affect their breathability or hand feel. The use of nanotechnology in the textile industry has increased rapidly due to its unique and valuable properties [62]. Polyacryloamidoxime fibers were successfully formed on the surface of polyacrylonitrile fibers using a hydroxylamine solution. Silver nano-clusters are identified by X-ray diffraction (XRD) and SEM microscopy. SEM observations reveal that the Ag nanoparticles were loosely arranged with a larger size distribution of 24.9 nm at pH=5, and a narrower size distribution of 23.5 nm at pH=7 at a reaction temperature of 30°C. Additionally, the size of the Ag nanoparticles increased to 29.8 nm as the reaction temperature increased to 60°C, indicating that temperature can accelerate the reduction of Ag+ into Ag faster than changing pH. The use of silver nanoparticles is also important, as several pathogenic bacteria have developed resistance against various antibiotics. Hence, silver nanoparticles have emerged up with diverse medical applications. The silver nanoparticles with their unique chemical and physical properties are proving as an alternative for the development of new antibacterial agents. The silver nanoparticles have also found diverse applications in the form of wound dressing, coating for medical devices, silver nanoparticles impregnated textile fabrics, Figure 7. The advantage of using silver nanoparticles is that there is continuous release of silver ions and the devices can be coated by both the outer and inner side thereby, enhancing its antimicrobial efficacy [63, 64].
Coating is a common technique used to apply nano-particles onto textiles. The coating compositions that can modify the surface of textiles are usually composed of nano-particles, a surfactant, ingredients and a carrier medium. The nano-particles are attached to the fabrics with the use of a padder adjusted to suitable pressure and speed, followed by drying and curing. The properties imparted to textiles using nanotechnology include water repellence, soil resistance, wrinkle resistance, anti-bacteria, anti-static and UV-protection, flame retardation, improvement of dyecability and i.e. Figure 8 illustrates silver nano particles [65].

Fig. 7: The reaction of silver ions with bacteria.

Fig. 8: Nano-particles of silver.

Rayleigh’s scattering theory stated that the scattering was strongly dependent upon the wavelength, where the scattering was inversely proportional to the wavelength to the fourth power. This theory predicts that in order to scatter UV radiation between 200 and 400 nm, the optimum particle size will be between 20 and 40 nm. TiO$_2$ nanoparticles have the potential to improve UV resistance, antistatic, as well as impart self-cleaning by photo-catalysis and thereby de-odor and antimicrobial effects [66].

Thermal properties of precursor polyacrylonitrile fibers containing nanoparticles of additives such as SiO$_2$, hydroxyapatite and montmorillonite have been examined. Based on the thermogravimetric curves, the coefficients of thermal stability of the fibers were found. It has been found that the thermal stability of PAN fibers is affected by the type of nano-additives and the value of the as-spun draw out ratio used during fiber spinning [67]. Polyacrylonitrile (PAN) nano-fiber mats were prepared by electro spinning and they were further modified to contain amidino diethylene diamine chelating groups on their surface via heterogeneous reaction with diethylene triamine (DETA). The aminated PAN (APAN) nano-fiber mats were evaluated for their chelating property with four types of metal ions, namely Cu(II), Ag(I), Fe(II), and Pb(II) ions. The amounts of the metal ions adsorbed onto the APAN nano-fiber mats were influenced by the initial pH and the initial concentration of the metal ion solutions. Increasing the contact time also resulted in a monotonous increase in the adsorbed amounts of the metal ions, which finally reached equilibrium at about 10 h for Cu(II) ions and about 5 h for Ag(I), Fe(II), and Pb(II) ions. The maximal adsorption capacities of the metal ions on the APAN nano-fiber mats, as calculated from the Langmuir model, were 150.6, 155.5, 116.5, and 60.6 mg g$^{-1}$, respectively. Lastly, the spent APAN nano-fiber mats could be facilely regenerated with a hydrochloric acid (HCl) aqueous solution [68].

Future outlook for functional finishing:

The new technologies such as nanotechnology, nano-fiber formation using electrospinning technique are promising approaches in the future for improving all textiles properties. Nanotechnology can provide high durability for fabrics, because nano-particles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function. In addition, a coating of nano-particles on fabrics will not affect their breathability or hand feel. It is expected that nanometal (silver, titanium and zinc e.g.) as well as its colloidal solution will be useful to give excellent antibacterial, anti-static anti-UV, water repellency, conductivity, fire-resistance and deodorant finish of acrylic fibers.

Plasma processes are characterized by the very small quantity of chemicals involved and by the
absence of solvent or water, which are usually employed in traditional finishing processes. Non-thermal plasma has been used extensively in biomedical applications; plasma technology seems to be good tool to alter the surface property, wettability, surface adhesiveness, electrical conductivity, antibacterial and dyability, and printability of the treated acrylic fibers.

The enzymatic modification of synthetic materials has immense potential both in the functionalization of bulk materials, such as polyacrylonitrile, polyamide or polyester, and in the production of polymers for specialty applications (e.g. for the production of medical devices and electronics). The major advantages of enzymes in polymer modification compared with chemical methods are milder reaction conditions and highly specific nondestructive transformations targeted to surfaces. The demand of applying this treatment in industrial sector can avoid hazardous chemical and save the environment.

Today’s textile industry makes use of microencapsulated materials to enhance the properties of finished goods. One application increasingly utilized is the incorporation of microencapsulated phase change materials (PCMs). Phase change materials absorb and release heat in response to changes in environmental temperatures. The property of microencapsulated phase change materials can be harnessed to increase the comfort level for users of sports equipment, military gear, bedding, clothing, building materials, and many other consumer products.

Many different active materials like drugs, enzymes, vitamins, pesticides, flavors and catalysts have been successfully encapsulated inside micro-balloons or microcapsules made from a variety of polymeric and non-polymeric materials including poly(ethylene glycol), poly(methacrylate), poly(styrene), cellulose, poly(lactide), poly(lactide-co-glycolide), gelatin and acacia, etc. These microcapsules release their contents at appropriate time by using different release mechanisms, depending on the end use of encapsulated products. This technology has been used in several fields including pharmaceutical, agriculture, food, printing, cosmetic, textile and defense.

Acrylic fibers are considered the most suitable precursor for making high performance carbon fibers. A study is aimed to understand the role played by acrylic fibre modification treatment in order to improve the carbon fibers properties. Porous carbons had been widely used as adsorbents, catalyst/catalyst supports, electronic material and energy storage material due to its higher surface area and larger pore volume.

Future studies can be boosted on some treatments on acrylic fibers waste to prepare carbon fibers and to obtain new composites as well as ion exchange for metal removal. Also, it is possible to recycle acrylic fibers in two stages as production waste and in the form of blends with natural polymer such as keratin outerwear and can be used for carpets and blanket.

References
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