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ФУНКЦИОНАЛИЗАЦИЯ И УЛТРАЗВУКОВО БАГРЕНЕ НА ПОЛИАКРИЛОНИТРИЛНИ НАНОВЛАКНА

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FUNCTIONALIZATION AND ULTRASONIC DYEING OF POLYACRYLONITRILE NANOFIBERS

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Abstract:

The physicochemical behavior of a polymer is fundamentally dictated by its backbone architecture and the nature of its pendant groups, making post-polymerization functionalization a critical strategy for synthesizing systems with optimized characteristics. While polyacrylonitrile (PAN) possesses excellent mechanical and thermal resilience, its hydrophobic nitrile (-CN) groups and high crystallinity often impede dye penetration, resulting in poor color retention. To overcome these limitations, researchers integrate additional monomers, graft functional groups such as polyethylenimine (PEI), or utilize a two-stage hydrolytic activation . In the latter approach, the electrophilic carbon center of the nitrile group is subjected to a progressive nucleophilic transition within a controlled alkaline environment. Spectroscopic analysis confirms that these groups hydrate into intermediate amides (-CONH2) before converting into negatively charged carboxylate (-COO-) sites.

This multi-step hydrolysis significantly increases the polymer's hydrophilicity and negative surface charge, turning a hydrophobic material into an anionic substrate suitable for heavy metal adsorption or enhanced dyeability. These carboxylate sites serve as high-affinity docking points for cationic dyes, facilitating strong ionic bonding rather than simple physical coating. To ensure deep dye penetration into these dense nanofibers meshes, advanced processing technologies like ultrasonic-assisted dyeing are employed, utilizing cavitation effects to preserve fiber integrity. Furthermore, precise control of parameters, such as maintaining a temperature of approximately 80°C, is essential to open the fiber microstructure while preventing the degradation of mechanical properties. By integrating these surface modifications with advanced techniques, it is possible to develop functionalized PAN nonwoven textiles with good color fastness and scalable application potential.

Keywords: *Polyacrylonitrile (PAN), Nanofibers, Nitrile Hydrolysis, Cationic Dyeing, Surface Activation*

1. Introduction and Chemical Modification Principles

Polyacrylonitrile (PAN) is a cornerstone polymer widely utilized in the production of high-performance technical yarns and electrospun nanofibers due to its excellent carbon yield, thermal stability, and mechanical strength. In membrane technologies (such as ultrafiltration), PAN is traditionally classified as a moderately hydrophilic or low-fouling polymer owing to the presence of polar nitrile (−C≡N) groups within its molecular chain. However, this inherent water affinity is often insufficient for advanced engineering applications, necessitating surface modification strategies—such as blending, plasma treatments, or chemical grafting—to enhance surface energy and wettability.

The high density of surface nitrile groups poses a distinct challenge for conventional aqueous coloration processes, as their hydrophobic nature and tightly packed semicrystalline structures act as a barrier to dye diffusion (1). Traditional immersion dyeing often yields poor dye exhaustion and surface-only staining that lacks washing durability (2). Consequently, developing precise surface modification techniques that introduce reactive dyeing sites without degrading the underlying polymer backbone is essential for developed functionalized textiles.

The chemical conversion of PAN from an inert matrix to a highly dyeable substrate typically proceeds via a multi-step alkaline hydrolysis process (3). When exposed to a strong base (such as NaOH) under controlled thermal conditions, the electrophilic carbon of the nitrile group undergoes progressive nucleophilic attack (4). This hydrolytic pathway proceeds through a systematic transition:

• Hydration Phase: The nitrile group (−C≡N) is first converted into an intermediate amide group (−$CONH_2$). This stage is generally characterized by a localized decrease in polymer crystallinity and an initial boost in water affinity.

•Conversion Phase: Continued alkaline exposure transforms these intermediate amides into negatively charged carboxylate groups (−COO−). This transition introduces permanent ionic anchors throughout the accessible polymer matrix, substantially increasing hydrophilicity and promoting swelling in aqueous solutions (3, 5) (Figure 1)

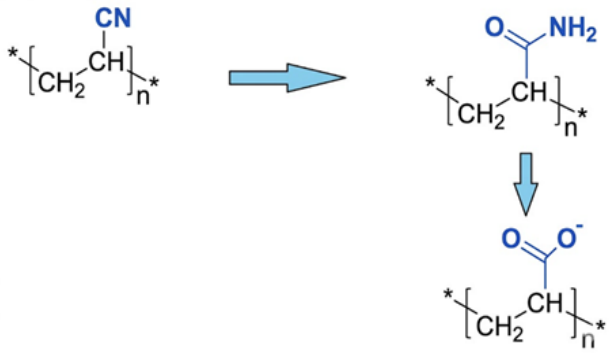


Figure 1. *Initial hydration step transforms the nitrile groups (Hydrophobic/Inert) into intermediate amides (Intermediate), and further converted into carboxylate groups (-COO-) (Hydrophilic/Anionic).*

To prevent the structural "melting," fusion, or complete degradation of delicate nonwoven electrospun fiber webs, the extent of this chemical transformation should be monitored. The progress of the reaction is quantitatively tracked using Fourier-Transform Infrared (FT-IR) spectroscopy, where successful modification is verified by the reduction of the sharp nitrile stretching vibration at 2240 cm^{-1} and the concurrent emergence of a broad carbonyl (−C=O) peak near 1730 cm^{-1} (5, 7).

Alternatively, researchers can bypass oxygen-based hydrolysis entirely through the structural integration of comonomers or via specialized chemical grafting. For example, functionalizing the polymer backbone by copolymerizing acrylonitrile (AN) with methyl acrylate (MA) and a cationic third monomer, such as 2-aminoethyl methacrylate hydrochloride (AMA), creates high-affinity docking frameworks reactive toward anionic dyes (such as C.I. Reactive Red 2) (Figure 2).

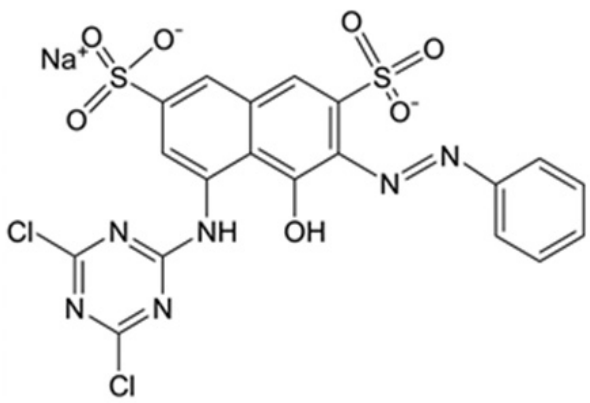


Figure 2. *Anionic dye (CI- Reactive Red 2)*

Similarly, grafting branched polymers like polyethylenimine (PEI) provides an alternative pathway. The amine groups of the PEI molecule act as strong nucleophiles that attack the hydrolysed nitrile carbons, generating a branched, nitrogen-rich architecture. PEI's primary and secondary amines act as nucleophiles to attack the electrophilic carbons on the pre-hydrolyzed PAN chains .This architecture establishes a highly dense population of positive ionic anchors suitable for coordinating a broad range of chemical dyes (6).(Figure 3)

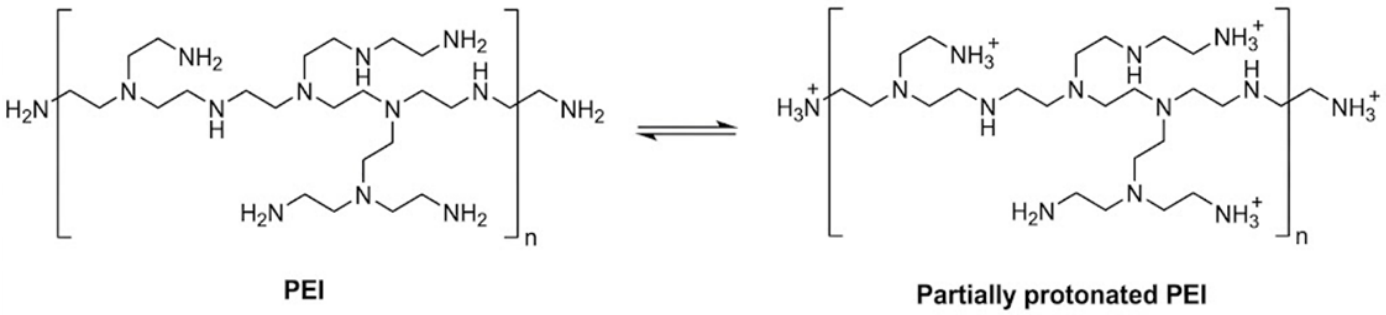


Figure 3. *Partial protonation of polyethylenimine*

2. Dyeing Mechanisms and Wastewater Remediation Applications

2.1 Cationic Dyeing

Once the surface nitrile groups of PAN are converted into anionic carboxylate sites, the fibers exhibit excellent affinity toward cationic (basic) dyes. The underlying coloration mechanism relies on robust electrostatic attraction, where the positively charged chromophore of the basic dye (D+) forms a durable ionic bond with the negatively charged carboxylate site (−COO−) on the modified polymer chain (8). (Figure 4)

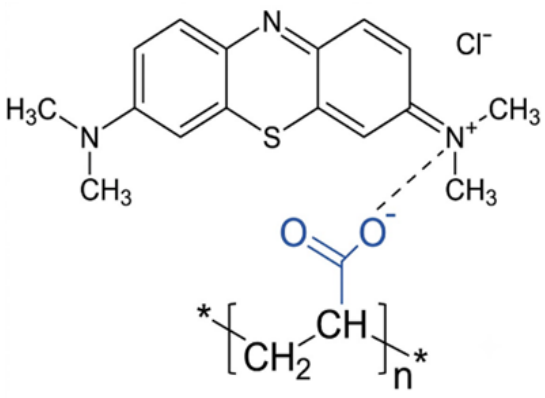


Figure 4*.Possible electrostatic interaction between Hydrolysed PAN & Methylene Blue (Basic Blue 9)*

These localized ionic linkages provide significantly higher wash- and light-fastness compared to the weak Van der Waals forces relied upon during disperse dyeing of untreated polymers.

The physical architecture of the textile substrate significantly influences the kinetics of both chemical activation and subsequent dye diffusion:

• Nanofibers: Because electrospun mats feature an enormous surface-area-to-volume ratio and high porous network density, the dye molecules reach active surface sites almost instantaneously. However, this high morphological sensitivity requires a lower concentration of alkali during the initial hydrolysis step to preserve structural web integrity.

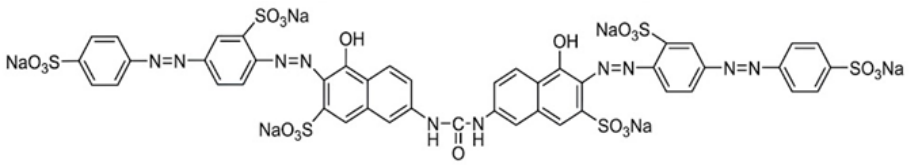
• Twisted Yarns: In compact, twisted PAN yarns, the chemical modifiers and dye liquors must penetrate deep into inter-fiber microspaces. The twist density directly limits the rate of chemical diffusion, requiring supplementary energy to achieve uniform coloration. To facilitate deep dye penetration without compromising fiber tensile strength, ultrasonic energy can be applied at elevated temperatures (e.g., 80°C). Sonication temporarily swells the polymer microstructure, resulting in high color yields (K/S values) even at low surface conversion levels (less than 15%) (9).

2.2 Anionic Dye Adsorption and Environmental Remediation

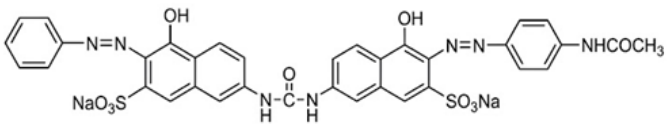
Beyond textile coloration, amine-functionalized PAN nanofibers serve as exceptional adsorbents for environmental remediation, particularly for the removal of anionic dyes from industrial wastewater (10). Electrospun PAN nanofiber webs can be chemically modified using various amine-containing compounds, including diethylamine (DEA), diethylenetriamine (DETA), and triethylenetetramine (TETA).

Attenuated Total Reflection (ATR) spectroscopy confirms that these amine groups successfully graft onto the fiber surface by reacting with the nitrile groups of PAN to form stable amide linkages. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) indicate that this functionalization increases surface roughness and introduces a highly intertwined fiber morphology driven by crosslinking.

Despite these structural alterations, the functionalized PAN (FPAN) nanofibers exhibit exceptional adsorption capacities for anionic model compounds, such as Direct Red 80 and Direct Red 23 (Figure .5) The total dye uptake is governed by operating parameters including initial pH, adsorbent dosage, contact time, and initial dye concentration. Equilibrium studies indicate that the adsorption behavior conforms to the Langmuir isotherm model, while the kinetic pathways adhere strictly to pseudo-second-order kinetics, rendering FPAN a highly scalable candidate for industrial wastewater treatment.



Direct Red 80



Direct Red 23

Figure 5. *Anionic dyes (Direct Red 80 and Direct Red 23)*

3. Conclusion

The conversion of inert nitrile groups into active ionic sites fundamentally transforms the surface functionalization of polyacrylonitrile substrates. By shifting the material from a hydrophobic state to a highly hydrophilic state with controllable zeta potentials, surface modifications open new pathways for advanced coloration and environmental applications. Combining precise chemical hydrolysis or amine grafting with auxiliary techniques like ultrasonic processing provides an efficient, scalable framework for producing vibrant, durable functional textiles and highly efficient wastewater treatment membranes.

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