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REVIEW ARTICLE

Beyond Fluorochemistry: A Critical Synthesis of PFAS-Free Water-Repellent Finishing for Applied Textiles

What the current evidence supports, where it disagrees, and what it means for fabric design and manufacturing

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ABSTRACT

The phase-out of long-chain per- and polyfluoroalkyl substances (PFAS) has pushed water-repellent finishing toward a crowded field of fluorine-free chemistries, yet the evidence base is fragmented across chemistries, substrates and test protocols. This editorial synthesis examines ten supplied source records covering alkyl-functional silanes and sol-gel systems [5] [7] [10], amino-alkyl polysiloxane-silica hybrids [4], cationic waterborne polyurethane/acrylate latexes [8], strongly cationic fluorine-free emulsions [2], bio-based fatty-acid polymers [3] [6], and hierarchical nanostructuring by nanogravure printing or nanoparticle infiltration [1] [9]. Across these records, two mechanisms recur: lowering surface energy with long alkyl chains, and adding micro- to nanoscale roughness that shifts wetting toward the Cassie-Baxter regime [1] [4] [9]. Reported durability ranges widely, from roughly ten wash cycles for some bio-based polymers [6] to 30 soaping rounds [4], 50 washes [8] and 65 wash cycles [9], but the records use different washing protocols, substrates and evaluation criteria, so these figures are not directly comparable. Several studies report contact angles of 130-150 degrees and spray ratings maintained after laundering [7] [8], while others emphasize abrasion and mechanical resilience [10]. Practical implications include substrate-specific formulation, attention to breathability and handle penalties, and the need for harmonized durability reporting before claims of fluorinated-performance parity can be treated as established.

Keywords: PFAS-free finishing; durable water repellency; superhydrophobic textiles; sol-gel coatings; wash durability; cotton and polyester finishing

SECTION 01

Why the comparison problem defines this field

The case for replacing PFAS in water-repellent textiles rests on environmental and health concerns rather than on demonstrated performance equivalence, and the supplied records make that distinction visible. Dignes and colleagues describe long-chain PFAS as historically offering superior breathable and flexible repellency while being persistent, bioaccumulative and associated with health impacts, which frames the search for alternatives as a performance-challenge problem rather than a simple substitution [9]. Hadhri and colleagues similarly situate their work within the phase-out of long-chain PFAS and the need for fluorine-free finishes that approach legacy performance [7]. This shared motivation is the strongest point of agreement across the literature supplied here.

The disagreement begins as soon as performance is quantified. Reported durability spans roughly ten washing cycles for stearic-acid-based polymers [6], 30 soaping rounds for a cross-linked polysiloxane-silica hybrid [4], 50 washes for a cationic waterborne polyurethane/acrylate [8], and 65 wash cycles for hierarchically nanostructured silica coatings [9]. These numbers

invite ranking, but the underlying tests differ in wash chemistry, mechanical action, temperature and the criterion used to declare failure, and the abstracts supplied do not permit normalization. A reader who treats 65 cycles as evidence that one chemistry outperforms another would be over-reading the record.

A second structural problem is substrate specificity. Cotton and polyester differ in surface charge, chemistry and intrinsic roughness, and the records treat them differently: cationic systems are argued to adsorb strongly to negatively charged cotton [2] [8], whereas roughness-spectrum analysis shows that initially smooth polyester gains most from submicrometer structuring while already-rough fabrics benefit less [1]. Any claim that a finish is generically 'PFAS-free and durable' therefore conceals the substrate dependence that product developers most need to know.

SECTION 02

Surface energy and roughness: two levers, unevenly evidenced

The mechanistic core of the supplied literature is consistent: water repellency is engineered by combining low-surface-energy alkyl chemistry with multiscale roughness. Szerlauth and colleagues formalize this through a roughness-spectrum analysis they call 'Wenzel spectroscopy,' showing that submicrometer topographic components move smooth polyester from the impregnated Wenzel regime toward or into the Cassie-Baxter state, raising contact angle by 5-10 degrees and reducing the pinning parameter [1]. Yu and colleagues describe an analogous synergy in which a cross-linked amino long-chain alkyl polysiloxane combined with modified silica creates a micro/nano multiscale rough structure on cotton [4]. Lin and colleagues tune silica layer morphology from smooth film to hierarchical structure by controlling methyltrimethoxysilane hydrolysis kinetics [5].

The roughness argument, however, is not uniformly supported across substrates. Szerlauth and colleagues explicitly report that initially rougher fabrics already in the Cassie-Baxter regime are less affected by nanostructuring [1]. This is an important boundary condition: the same topographic intervention that rescues a smooth fabric may add cost and process complexity to a fabric that did not need it. The practical corollary is that roughness engineering should be specified per substrate and weave, not adopted as a universal step.

Surface chemistry choices are similarly diverse and only partly comparable. Octylsilane in an amino-functional silicone dispersion yields static contact angles of 130 degrees on cotton and 145 degrees on polyester [7]; long-alkyl-chain silane functionalization of infiltrated silica nanoparticles underpins a hierarchical nanocoating [9]; and a molecularly assembled silica shell is described as covalently bonded to individual yarn fibers without discrete nanoparticles or fluorinated chemistry [10]. These are different architectures-particulate, sol-gel and fiber-level covalent-and the supplied abstracts do not contain the side-by-side data needed to rank them on either repellency or cost.

SECTION 03

Durability claims: encouraging signals, weak comparability

Durability is where the literature is most assertive and least commensurable. Hadhri and colleagues report that after five ISO 105-C10 wash cycles their treated cotton and polyester retained a spray rating of 5/5 and AATCC 193 grade 7, equalling or outperforming a fluorinated control, with no more than 5% loss of water-vapour permeability and only a marginal increase in bending stiffness [7]. This is among the more informative records because it benchmarks against a fluorinated finish and reports comfort-related properties alongside repellency. Jiang and colleagues report a static water contact angle of 142 degrees after 50 washes for a cationic waterborne polyurethane/acrylate on cotton [8], and Dignes and colleagues report consistent superhydrophobic performance after 65 wash cycles [9].

Mechanical durability is addressed by fewer records but is arguably more demanding. Liu and colleagues claim that their covalently bonded fluorine-free silica shell endures intensive abrasion, high-velocity water impacts, steam exposure and extreme temperature cycles, and they argue that conventional nanoparticle assemblies or PFAS finishes tend to detach or degrade under abrasion [10]. This directly challenges the durability narrative of particulate approaches [9] and of nanoparticle-containing hybrids [4], although the supplied abstracts do not contain a common abrasion protocol that would

settle the question. The honest reading is that multiple architectures can be made durable, but the field lacks a shared stress-test standard.

Bio-based chemistries occupy a distinct position. Sharif and colleagues report water repellency rating 4 and oil repellency rating 1 with washing durability up to 10 cycles, and note that after 20 cycles water repellency persisted only for ironed fabric and oil repellency fell to zero, while results were comparable to or better than a commercial C6-based fluorocarbon [6]. An earlier stearic-acid/citric-acid system reported appreciable oil and water repellency plus crease recovery, soil resistance, antimicrobial performance and shrinkage [3]. These are broader property claims than the silane and polyurethane records, but the durability ceiling is lower, and the multi-property framing makes it harder to isolate which effect drives repellency.

SECTION 04

Comfort, hand and the hidden cost of repellency

Water repellency is only commercially useful if the fabric remains wearable, and the supplied records treat this unevenly. Yang and colleagues report that finished cotton largely retains its original whiteness (untreated woven cotton near 95) and that air permeability falls by only 10-30% due to pore blockage and structural rearrangement, which they characterize as maintaining excellent breathability [2]. Yu and colleagues state that air permeability, mechanical properties and whiteness are hardly affected after finishing [4]. Hadhri and colleagues quantify a water-vapour transmission loss of no more than 5% and a marginal bending-stiffness increase [7].

These are reassuring but not equivalent measurements. Air permeability, water-vapour transmission and bending stiffness capture different aspects of comfort, and none of the supplied abstracts reports a standardized sensory hand assessment. The 10-30% air-permeability reduction reported by Yang and colleagues [2] is notably larger than the 'hardly affected' language used elsewhere [4], which may reflect different add-on levels, different fabrics or different measurement conditions rather than a genuine contradiction. Product developers should treat comfort claims as formulation- and add-on-dependent until comparable data are available.

A related uncertainty concerns whiteness and appearance, which matter for apparel and technical textiles alike. Only two records address it explicitly, and both report limited change [2] [4]. The absence of appearance data in the remaining records is a gap rather than evidence of no effect.

SECTION 05

Manufacturing routes: scalability asserted more often than demonstrated

The records propose several routes with different implications for industrial adoption. Pad-dry-cure is used for the polysiloxane-silica hybrid [4], the octylsilane sol-gel system [7] and, in pad-curing form, the waterborne polyurethane/acrylate [8]; these are familiar wet-finishing operations and therefore the least disruptive to existing lines. Lin and colleagues describe a one-step dip-coating from water-based methyltrimethoxysilane solutions with hydrophobicity tuned by pH and reaction time [5], and Liu and colleagues describe a one-step molecular assembly compatible with a wide range of natural and synthetic fibers [10]. Szerlauth and colleagues use nanogravure printing, which they describe as inherently scalable, to impose submicrometer topography on polyester [1].

Scalability claims should be read cautiously. Nanogravure printing [1] and multistep nanoparticle infiltration with subsequent surface functionalization [9] involve more process steps than pad-dry-cure, and the supplied abstracts do not report line speed, energy use, chemical consumption, waste streams or cost. The repeated use of the word 'scalable' across records [1] [7] [10] is an authorial assertion about process compatibility, not a demonstrated manufacturing outcome. For manufacturing specialists, the more decision-relevant distinction is between aqueous, water-borne systems that fit conventional padding [5] [7] [8] and architectures that require new deposition equipment [1] [9].

Chemistry selection also carries supply-chain and formulation implications that the records only gesture toward. Cationic emulsions with small particle size and narrow distribution are argued to give stronger electrostatic adsorption and more uniform film formation on cotton, which the authors link to washing and abrasion resistance [2]. If that mechanism is robust, formulation variables such as charge density and polydispersity become first-order manufacturing controls rather than secondary details.

SECTION 06

What remains unresolved

Three uncertainties stand out. First, the evidence does not establish parity with fluorinated finishes across the property set that matters commercially. Hadhri and colleagues report equalling or outperforming a fluorinated control on spray rating and alcohol repellence after five washes [7], and Sharif and colleagues report comparability with a C6-based fluorocarbon [6], but these are isolated comparisons on specific substrates and protocols, not a general finding. Second, oil repellency is consistently harder to achieve than water repellency in fluorine-free systems: the bio-based polymers reached oil repellency rating 1 and lost it entirely after 20 cycles [6], and several silane and polyurethane records report water repellency without claiming oil repellency [5] [8] [10]. Where oil resistance is a functional requirement, the fluorine-free evidence base is thin.

Third, the environmental case for specific alternatives is largely outside the supplied records. The abstracts justify substitution by reference to PFAS persistence, bioaccumulation and health effects [9] and to regulatory pressure [3] [7], but none of them reports a comparative life-cycle assessment, toxicity profile or biodegradation study for the replacement chemistries. Readers should therefore distinguish the well-supported claim that PFAS-free finishes can deliver useful water repellency from the unsupported claim that any particular alternative is environmentally preferable across its life cycle.

A further unresolved issue is the relationship between laboratory repellency metrics and field performance. Contact angle, spray rating and AATCC 193 grades are reported extensively [1] [7] [8], but the records do not connect these to garment-level performance in rain, flexing, soiling or repeated domestic laundering. The gap between a 150 degrees contact angle [8] and a satisfied end user is not addressed by the supplied evidence.

SECTION 07

Implications for applied textile design and manufacturing

For design teams, the most defensible implication is substrate-first selection. Because nanostructuring benefits smooth fabrics far more than already-rough ones [1], and because cationic systems are argued to depend on electrostatic affinity to cotton [2] [8], a finish should be chosen together with the base fabric rather than specified as a standalone chemical. Polyester and cotton may reasonably receive different architectures, and blends-absent from the supplied records-should be treated as unproven territory.

For manufacturing, the records support a staged adoption logic. Aqueous pad-dry-cure systems based on alkylsilane sol-gel [7], polysiloxane-silica hybrids [4] or cationic polyurethane/acrylate latexes [8] offer the shortest path because they use existing wet-finishing equipment, with reported wash durability ranging from 30 soaping rounds [4] to 50 washes [8]. Higher-durability claims associated with nanoparticle infiltration [9] and covalent fiber-level shells [10] are attractive but imply additional process steps whose industrial cost is not documented in the supplied records. Nanogravure printing [1] should be regarded as a promising but equipment-specific route.

For specification and quality control, the practical recommendation is to demand protocol-matched durability data rather than headline wash-cycle counts. Buyers should ask which wash standard, substrate, add-on level and failure criterion produced a given claim, and should require comfort metrics-air permeability, water-vapour transmission and bending stiffness-alongside repellency [2] [4] [7]. Where oil repellency is required, current fluorine-free options should be qualified with particular caution given the low and non-durable oil ratings reported for bio-based systems [6]. Finally, because no supplied record provides a life-cycle or toxicity comparison of the alternatives, environmental claims should be limited to the absence of PFAS unless further evidence is generated.

CONCLUSION

Conclusions

The supplied records show that PFAS-free water-repellent finishing is technically feasible across several distinct architectures: alkylsilane and sol-gel systems [5] [7], polysiloxane-silica hybrids [4], cationic polyurethane/acrylate latexes [8], bio-based fatty-acid polymers [3] [6], and hierarchical or covalent nanostructured coatings [1] [9] [10]. The convergent mechanistic insight is that low-surface-energy alkyl chemistry combined with controlled multiscale roughness drives wetting toward the Cassie-Baxter state, with the greatest benefit on smooth substrates [1] [4]. The convergent weakness is evidentiary: durability is reported against different wash protocols and criteria, ranging from about ten cycles [6] to 65 cycles [9], and scalability is asserted rather than demonstrated. Fluorinated-performance parity is suggested by isolated benchmarked studies [6] [7] but not established generally, and oil repellency remains the least secure property [6]. The defensible position for applied textile development is therefore substrate-specific formulation, preference for aqueous processes compatible with existing pad-dry-cure lines where durability requirements permit [4] [7] [8], explicit comfort specifications [2] [7], and restraint in environmental claims beyond PFAS elimination until comparative life-cycle and toxicity evidence exists.

SCOPE

Limitations

This review is based solely on the ten supplied source records, which are abstracts rather than full texts; methodological details, statistical analyses, exact test standards and raw data were not available for verification. The records cover a narrow set of substrates, principally cotton and polyester, and do not address blends, wool, regenerated cellulosics or nonwovens. Durability figures are not comparable because washing protocols, mechanical action and failure criteria differ and are not fully described. Several performance and scalability statements are authorial claims rather than independently replicated findings, and no record supplies life-cycle, toxicity or biodegradation data for the replacement chemistries. No systematic-review methodology was used, no quantitative pooling was attempted, and the synthesis should be read as a critical editorial interpretation of a limited evidence sample rather than a comprehensive or exhaustive assessment.

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