

DOI: 10.19884/j.1672-5220.202311009

Review of Antifouling Finishing of Textiles: Theme, Evolution and Fabrication Methods

DING Fengmei^{1,2}, GUO Yali^{1,2}, WANG Qingmiao³, WANG Xuehui^{1,2}, WANG Ping³, XING Zhiqi¹, CHEN Luyi^{4*}

1. College of Chemistry and Chemical Engineering, Donghua University, Shanghai 201620, China

2. National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 201620, China

3. Youngor Group Co., Ltd., Ningbo 315153, China

4. Shanghai Research Center for Reform and Development of State-Owned Assets and State-Owned Enterprises, Shanghai 200233, China

Abstract: Antifouling textiles have been a hot research field in the last ten years. But lately, the European Union (EU) is expected to ban the production of C6 fluorinated water repellent, oil repellent and antifouling agents from 2025, achieving complete fluoride-free antifouling measures. In the context of the current policy regulations on fluorine-free treatment in the waterproof, oil repellent and antifouling finishing field, this paper conducts a literature survey and comprehensive understanding of the current research status and trend in fluorine-free antifouling finishing. CiteSpace and Carrot2 are used to conduct a literature review of the latest papers in two databases, Web of Science (WoS) and China National Knowledge Infrastructure (CNKI). Firstly, the theoretical evolution and technical characteristics of textiles antifouling finishing technology are systematically discussed, and the technological differences of antifouling finishing textiles for different demands are compared. Secondly, the three main stages of the development of textile antifouling finishing technology and its corresponding finishing methods are summarized. Finally, three paths for the future development of fluorine-free antifouling finishing are prospected: construction of low surface energy, construction of uniform rough surface and low surface energy, and construction of multistage rough surface with low surface energy. To facilitate the transition of the industrial sector to fluorine-free, regulatory restrictions could be strengthened by enhancing the sampling inspection of apparel fabrics, detecting fluorine in wastewater discharges and restricting the production of fluorine-containing finishing agents by manufacturers.

Key words: antifouling finishing; fluorine-free; hydrophobicity; oleophobicity; surface roughness

CLC number: TS1

Document code: A

Article ID: 1672-5220(2024)06-0616-14

Open Science Identity
(OSID)



0 Introduction

With the rapid development of the economy and the continuous improvement of people's living standards, there is a growing demand for functional textiles^[1], such as antibacterial^[2], flame retardant^[3], anti-wrinkle^[4] and antifouling^[5], which leads to the extensive research about various functions.

Antifouling textiles are not contaminated easily by water and oil, dry dust or particles during use. For many kinds of textiles, it's common to achieve antifouling by water repellent finishing and oil repellent finishing. Water repellent textiles are obtained by chemical reagent finishing to lower the surface tension of the fabric, thus preventing water droplets from wetting the fabric^[6]. Oil repellent finishing makes the surface tension of the fabric lower than that of various oils so that oil on the treated fabric beads and does not wet the fabric. Antifouling is the ability to remove dirt easily by ordinary washing or wiping methods after the fabric is contaminated. The overview diagram of the antifouling finish is shown in Fig. 1.

For a long time, researchers have mainly used fluorine-containing finishing agents to obtain good antifouling textiles. Fluorine-containing finishing agents dominate the market despite their toxicity. Typical fluorine-containing finishing agents, such as those based on perfluorooctanoic acid (PFOA) and perfluorooctane sulphonate (PFOS), have metabolites that are highly bio-accumulation^[7] and persistence. Once taken up, they combine with protein or plasma

Received date: 2023-11-22

Foundation items: Fundamental Research Funds for the Central Universities, China (No. 2232021G-03); National Natural Science Foundation of China (Nos. 72074132 and 71704165)

* Correspondence should be addressed to CHEN Luyi, email: cae_chenluyi@163.com

Citation: DING F M, GUO Y L, WANG Q M, et al. Review of antifouling finishing of textiles: theme, evolution and fabrication methods[J]. *Journal of Donghua University (English Edition)*, 2024, 41(6): 616-629.

protein in the blood and are hard to be decomposed through metabolism, resulting in liver, nerves,

immune, endocrine and reproductive toxicity of biology.

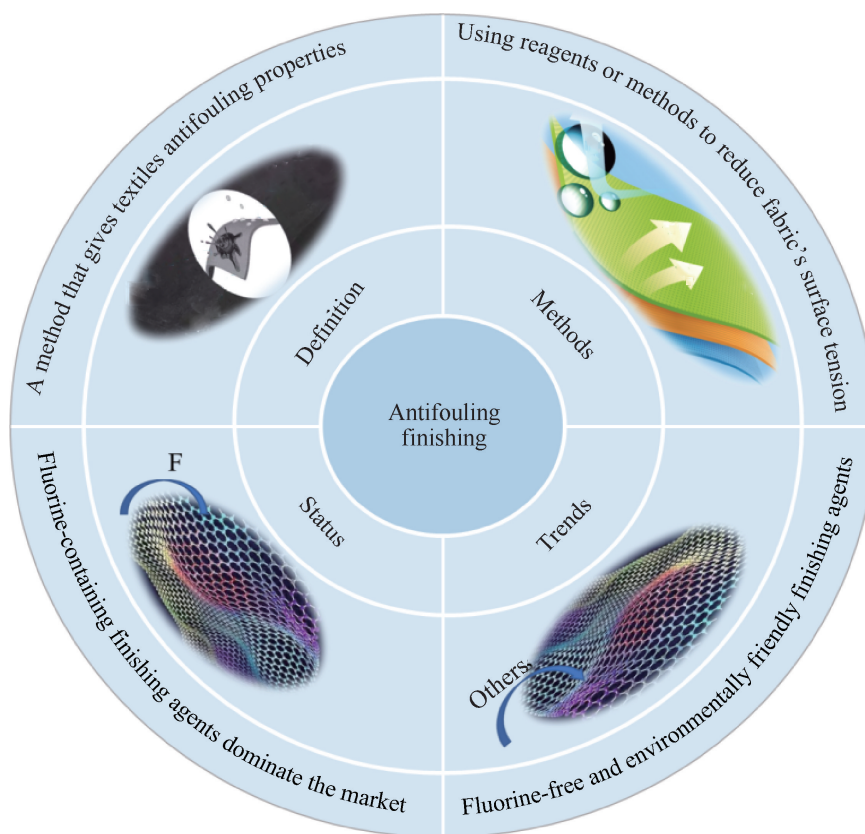


Fig. 1 Overview diagram of antifouling finishing

The vivo mass concentration of fluoropolymers with short carbon chains achieving 2 mg/kg leads to death^[8]. It has been proved that fluoropolymers with short carbon chains also possess great environmental toxicity and human health hazards. The European Union (EU) has issued a regulation concerning the production of short-chain perfluorocarbons (PFCS) with less than or equal to six fluorocarbon atoms. According to the regulation, the mass concentration of PFOA-related substances, either as intermediates or final products, should be no more than 20 mg/kg, indicating the restriction on intermediates in the production of short-chain PFCS. Therefore, it is urgent to develop fluorine-free finishing agents to replace fluorine-containing finishing agents. EU is expected to ban the production of short-chain PFCS with six fluorocarbon atoms (C6) finishing agents from 2025, achieving complete fluorine-free antifouling measures. The fluorine-free waterproofing agent is more environmentally friendly. However, compared with the fluorine-containing finishing agent, a large dosage is generally needed and no oil repellent effect is achieved, leading to poor antifouling properties of the fabric^[9]. The development of fluorine-free finishing agents should not

only conform to the current trend of ecological protection, but also need to ensure safety and antifouling. Therefore, developing fluorine-free, environmentally friendly and efficient textile antifouling finishing technologies has been an issue to be resolved in the textile industry.

In this review, the relevant literature in the field of textile antifouling finishing in recent years is analyzed and visualized. The theoretical evolution, technical characteristics and research progress of textile antifouling finishing are reviewed, and the focuses are on the three development stages and the corresponding technical characteristics. The development trend of fluorine-free finishing technology in the future is anticipated, thereby serving as a reference for the development of fluorine-free finishing technology.

1 Overview of Research Progress of Antifouling Finishing

To summarize the literature more comprehensively, key word search is conducted in databases of Web of Science (WoS) and China National Knowledge Infrastructure (CNKI), where “antifouling finishing”,

“water repellent finishing”, “oil repellent finishing”, “fluorine-free” and “superhydrophobic” are the key words. The search results were filtered by years and journals to get high-quality literature and 63 articles were finally selected, which involved journals of *Progress in Organic Coatings*, *ACS Applied Materials & Interfaces*, etc., as shown in Table 1.

Table 1 Literature numbers in different journals

Journal	Literature number
<i>Progress in Organic Coatings</i>	7
<i>ACS Applied Materials & Interfaces</i>	6
<i>Journal of Materials Chemistry A</i>	6
<i>Chemical Engineering Journal</i>	5
<i>Langmuir</i>	5
<i>Scientific Reports</i>	4
<i>Polymers</i>	4
<i>Cellulose</i>	4
<i>Nature Sustainability</i>	4
<i>Industrial Crops and Products</i>	3
<i>Applied Surface Science</i>	3
<i>Journal of Donghua University (English Edition)</i>	2
<i>Journal of Materials Science</i>	2
<i>ACS Sustainable Chemistry & Engineering</i>	2
<i>ACS Omega</i>	2
<i>Journal of Alloys and Compounds</i>	2
<i>Surfaces and Interfaces</i>	1
<i>Surface & Coatings Technology</i>	1

As can be seen from Table 1, *Progress in Organic Coatings* has the highest number of publications in the antifouling field. In *Progress in Organic Coatings*, seven papers are mainly related to hydrophobic surface achieved by coating which is simple to operate by impregnation, brush coating or spraying. In this way, the substrate surface can achieve hydrophobic, oil repellent, antifouling and other functions, but the disadvantages are that the fastness and hand feeling are not good enough. *ACS Applied Materials & Interfaces* is the journal with the second highest number of relatively related publications, and the related research is more focused on the surface energy of the substrate, where reducing the surface energy of the substrate is the key to obtaining the hydrophobic and antifouling properties.

1.1 WoS literature analysis

Figure 2 is the key word cluster analysis of WoS in

the field of antifouling textiles, and numbers in parentheses represent the frequency. The key words mainly include superhydrophobic, cotton fabric, oil-water separation, antifouling and fluorine-free. It can be seen that the currently researching hotspot is mainly to reduce the surface energy of the substrate through the fluorine-free route to obtain the waterproof and antifouling performance. Many researchers are committed to the superhydrophobicity of fabric and oil-water separation, and some progress has been made. However, the fluorine-free oil repellent of fabrics is still a difficult point, which remains unsolved.

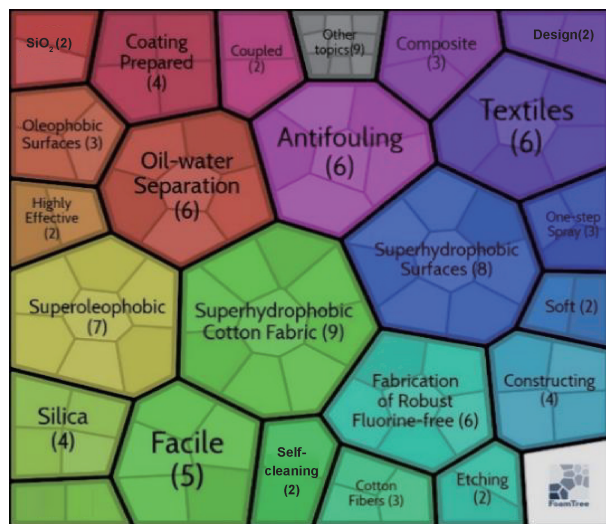


Fig. 2 Key word cluster analysis of WoS in the field of antifouling textiles

Figure 3(a) shows the key word analysis of WoS in the antifouling textile field in the recent ten years based on CiteSpace, and the recent research hotspots are visually exhibited. One node in Fig. 3 represents one key word and the size of the node reflects the number of articles containing these key words in the field of antifouling textiles. The connection between nodes represents the relationship between key words. It can be seen from Fig. 3(a) that the main key words are coatings, fabric, oil-water separation, and so on. Among these, the nodes of oil-water separation and coatings are the largest, indicating that coatings are a very important method for antifouling fabric. In Fig. 3(b), the map of the main author cooperation networks in this field shows that the cooperative relationships among scholars are scattered, which are mainly within certain institutions, and only a few scholars have close cooperative relationships. In the largest cooperation network, Visco, De Leo, Trovato, et al., published many papers focusing on superhydrophobic, oil-water separation fabric, and so on.

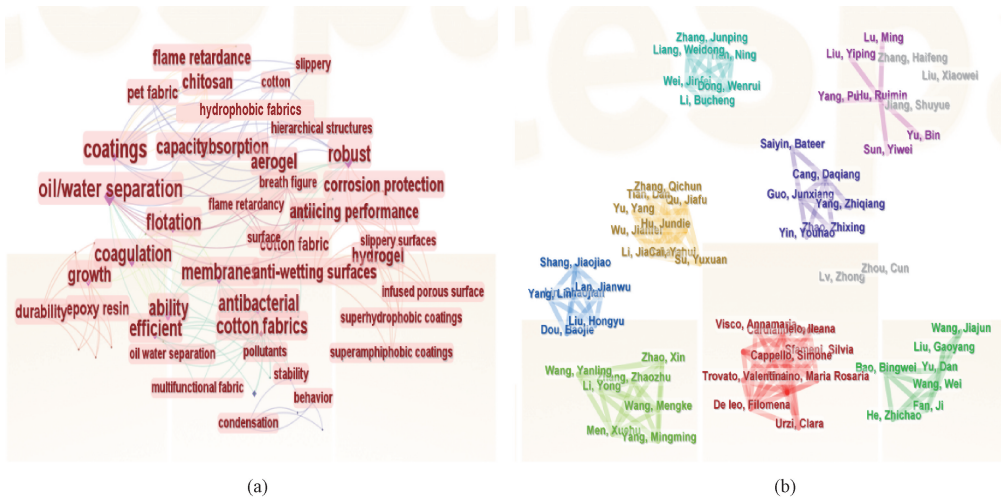


Fig. 3 Key word analysis and main author collaboration map of WoS: (a) key word analysis diagram; (b) main author collaboration map

1.2 CNKI literature analysis

Figure 4 (a) is based on the CiteSpace analysis of key words from CNKI concerning antifouling textiles in the recent ten years. As can be seen from Fig. 4(a), the main key words are superhydrophobic, antifouling performance and cotton fabric, suggesting that these are the most popular research topics in the antifouling textile field. The connections among the key words are

complicated, indicating their complex relationship. Figure 4 (b) shows the cooperation network map of the main authors in China, with close connections among scholars. It can be seen that in the largest cooperation network, Xu Lihui, Wang Liming, Shen Yong, et al., from Shanghai University of Engineering Science, have published many articles about superhydrophobic fabric.

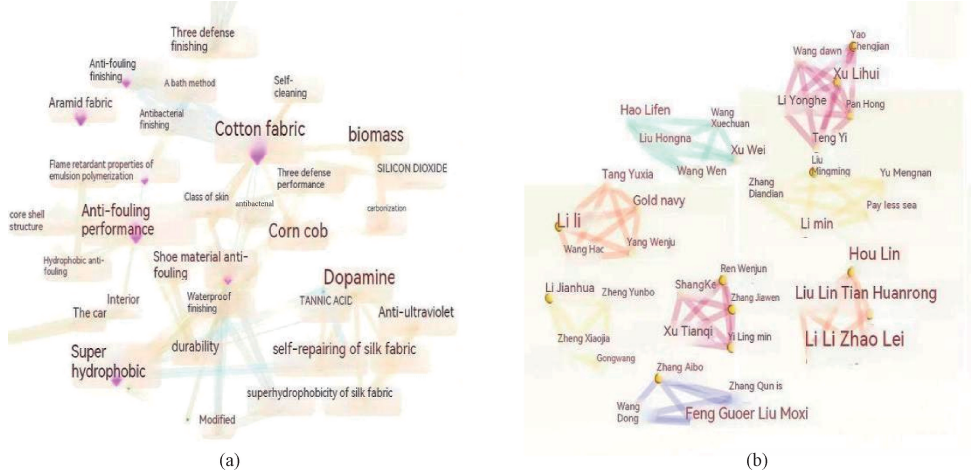


Fig. 4 Key word analysis and main author collaboration map of CNKI: (a) key word analysis diagram; (b) main author collaboration map

Based on the above analysis of the literature about antifouling textiles, it can be seen that superhydrophobicity, antifouling finishing of textiles and oil-water separation textiles are still hot topics of research.

2 Theoretical Evolution and Feature Recognition of Antifouling Finishing Technology

The theoretical basis of antifouling finishing needs to be clearly understood to obtain better antifouling performance of substrates. Herein, the evolution of the

theoretical basis and the corresponding feature recognition of antifouling finishing technology are briefly reviewed.

After many years of development, the basic theories of water repellent, oil repellent and antifouling finishing mainly include Young’s equation, Wenzel model and Cassie-Baxter model. To quantitatively evaluate the low surface energy interface, Thomas Young put forward Young’s equation in 1805 based on a lot of basic research, and defined the concept of contact angle (CA) θ [10]. The surface energy of the substrate was evaluated by the CA between the droplet and the substrate. Based on Young’s equation, researchers in this field found that the calculated results of this equation could not elucidate

non-smooth surfaces. It indicates that this equation is only applicable to smooth surfaces. Based on the above study, Robert amended Young's equation^[11] to propose the roughness factor R in 1936, which represented the change of the contact area between the droplet and the solid substrate caused by the change of roughness, and then the CA was changed. Thus, Wenzel model was established. Since then, not only surface tension but also the roughness of solid surfaces has been considered in antifouling finishing. Therefore, many researchers have conducted extensive and detailed studies on the relationship between surface roughness and surface energy of substrates^[11]. Wenzel model has made epoch-making progress in the study of surface properties of materials. However, there are defects in Wenzel model as well. In

the subsequent research, it is found that Wenzel model is only suitable for the homogeneous rough structure of solid surfaces and the non-homogeneous rough structure of solid surfaces with grooves embedded with air could not be accurately described. Accordingly, in 1944, Cassie and Baxter proposed Cassie-Baxter model which described the CA and non-homogeneous rough structure of a solid surface^[5]. Cassie-Baxter model can better explain the complex rough structure of solid surfaces to evaluate the surface properties and lays a theoretical foundation for the subsequent study of superhydrophobic surfaces. Till now, Wenzel model and Cassie-Baxter model have been utilized to reasonably describe and evaluate the rough structure of solid surfaces. The application of these theories are shown in Fig. 5.

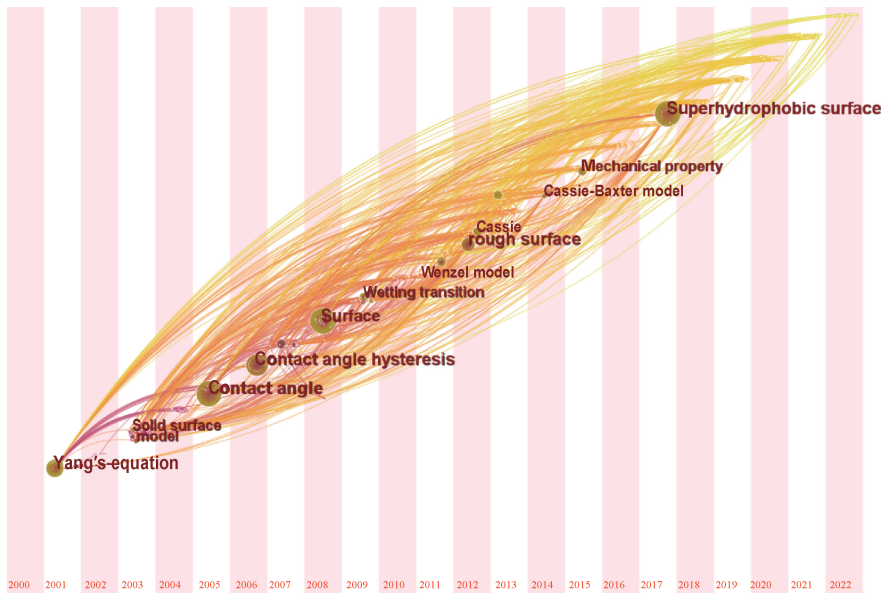
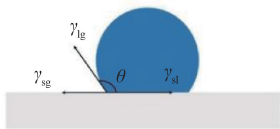




Fig. 5 Schematic diagram of application of antifouling finishing technology theory

Based on the theoretical evolution sequence of antifouling finishing technology, Young's equation,

Wenzel model and Cassie-Baxter model were compared in detail, as shown in Table 2.

Table 2 Theoretical evolution of antifouling finishing technology

Item	Theoretical model		
	Young's equation	Wenzel model	Cassie-Baxter model
Developing year	1805	1936	1944
Schematic of the model			
Application	Absolutely smooth and uniform surface	Homogeneous rough surface	Non-homogeneous rough surface
Equation	$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} \cos \theta$	$\gamma_{lg} \cos \theta = r(\gamma_{sg} - \gamma_{sl})$ $\cos \theta_w = r \cos \theta$	$\cos \theta = f_s \cos \theta_s + f_v \cos \theta_v$ $\cos \theta = r f_s \cos \theta_s + f_v \cos \theta_v$

(Table 2 continued)

Item	Theoretical model		
	Young's equation	Wenzel model	Cassie-Baxter model
Formula interpretation	γ_{sg} — surface tension of solid-gas contact surface; γ_{sl} — surface tension of solid-liquid contact surface; γ_{lg} — surface tension of gas-liquid contact surface; θ — CA	θ_w — apparent CA; r — roughness factor	θ — CA; r — roughness factor; θ_s — CA between solid and gas; θ_v — CA between liquid and gas; f_s, f_v — area fractions of the solid-liquid and gas-liquid interface per unit surface area, respectively, and $f_s + f_v = 1$
Determination of interface properties by θ	If $\theta < 90^\circ$, the solid surface is hydrophilic; if $\theta \geq 90^\circ$, the solid surface is hydrophobic; if $\theta \geq 150^\circ$, the solid surface is superhydrophobic	If $0^\circ < \theta_w < 90^\circ$, the solid surface is hydrophilic; if $90^\circ \leq \theta_w \leq 180^\circ$, the solid surface is hydrophobic	If $0^\circ < \theta < 90^\circ$, the solid surface is hydrophilic; if $90^\circ \leq \theta \leq 180^\circ$, the solid surface is hydrophobic
Antifouling characteristics	Surface tension	Homogeneous rough surfaces and surface tension	Non-homogeneous rough surfaces and surface tension

Young's equation reveals the relationship between the CA and the surface tension of the solid and liquid. It can be seen that reducing the solid surface tension is very important for the water repellent, oil repellent and soil repellent properties of the solid surface. Wenzel model indicates that the apparent CA will change along with the changed roughness, thus the hydrophilic and hydrophobic properties of the solid surface will be changed. Therefore, the roughness of the solid surface will affect the hydrophilic and hydrophobic properties greatly^[12]. Cassie-Baxter model reveals the influence of non-homogeneous rough structure and surface tension on the CA, namely, the larger the roughness of the solid surface, the more air components in the rough structure, and thus the larger the CA of liquid on the solid surface. Currently, Wenzel model and Cassie-Baxter model are widely accepted. In practice, due to the difficulty in estimating the roughness of the solid surface, it is necessary to analyze the specific experimental results to determine which experimental model it belongs to.

In conclusion, based on Young's equation, decreasing the surface tension of the solid surface to less than that of water and oil can make it water and oil repellent. Wenzel model and Cassie-Baxter model show that the roughness of a solid surface can be combined with reducing surface tension, to obtain good antifouling performance of a solid surface. Based on the above theories, many new technologies have emerged to make superhydrophobic, oil-water separation^[13] and self-cleaning^[14] fabrics. At present, there are few technologies to make textiles oil repellent and oil-fouling repellent except for using fluorine-containing finishing agents. More researchers are committed to reducing the surface tension of the substrate along with constructing the surface roughness of the substrate, and developing fluorine-free oil repellent or oil-fouling repellent finishing

technologies.

3 Comparison of Antifouling Finishing Technologies for Different Interface Characteristic Requirements

Based on the above overview of the theoretical evolution and feature recognition of antifouling finishing technologies, it can be seen that with the gradual in-depth research on the essential characteristics of water and oil repellent properties on different surfaces, different antifouling finishing technologies have been developed accordingly.

3.1 Methods of constructing low surface-energy surfaces

3.1.1 Fluorine-containing finishing agent

To reduce the surface energy of the fabric surface, fluorocarbon polymers were developed. It is believed that the electronegativity of fluorine atoms plays an important role in reducing the surface energy of fabrics. In perfluorine molecules, fluorine atoms form a "protective sleeve" to prevent chemical erosion. In perfluorinated polymers, low interchain forces, tight packing of perfluorinated polymer side chains and chain rigidity help to reduce surface energy. Therefore, the surface tension of fluorine-treated textile surfaces is lower than that of water (72.8 mN/m)^[15] and oil (20.0–30.0 mN/m), so that the textile is not easily stained by water and oily dirt wetting. For a long time, fluorine-containing finishing agents have been used to reduce the surface tension of fabrics to obtain excellent oil repellent and antifouling properties.

It has been studied that long carbon chain fluorine-containing finishing agent (C8) is degraded into PFOA and PFOS, which are biologically accumulating and strongly persistent to cause great harm to the human body

and environment. Accordingly, fluorine-containing finishing agents of C8 and longer fluorocarbon chains have been prohibited. Short chains of fluorine-containing finishing agents are the replacement^[16]. Yang et al.^[17] used C6 antifouling finishing agent E100 to treat the cotton fabric. The study showed that when the mass concentration of E100 was 60 g/L, the mass concentration of the crosslinking agent was 10 g/L, pH value was 6 and the rolling rate was 80%, the treated fabric possessed oil repellent grade of 5 and antifouling grade of 4–5. Dong et al.^[18] coated arylon fibers with fluorinated TiO₂ nanotubes to establish a superhydrophobic hollow TiO₂ nanotube network structure, thus a breathable, ultraviolet (UV) resistant and superhydrophobic coating with a CA of up to 152.0°–160.0° was created. Qian et al.^[19] synthesized a short-chain fluorinated copolymer emulsion through microemulsion polymerization using fluoroacrylate (C4F), glycidyl methacrylate (GMA), octadecyl acrylate (SA) and butyl acrylate (BA) as the copolymer. The water CA of the treated fabric was 157.0°, and the olive oil CA and the hexadecane CA were 148.0° and 128.0°, respectively, with a molar ratio of C4F to SA of 2 : 1. Li et al.^[20] synthesized amphiphilic triblock azide copolymers containing polyethylene glycol (PEG) and poly(2,2,3,4,4-butyl hexafluoroacrylate) blocks by reversible addition-fragmentation chain transfer (RAFT) polymerization, and the cotton fabric accordingly prepared exhibited a water CA of up to 155.0° and had good water repellent. Li et al.^[21] synthesized short-chain perfluorinated acrylate emulsion by perfluorinated butyl ethyl methacrylate (FA), vinylidene chloride (VDC), SA and N-hydroxymethylacrylamide (N-MAM). When the mass concentration of perfluorinated acrylate emulsion was 20 g/L, the coated cotton fabric possessed excellent water repellent and oil repellent properties, with water repellent grade of 4+ and oil repellent grade of 6. Gou et al.^[22] successfully prepared paraffin microcapsules with tetraethyl orthosilicate and fluorosilicate as shells and then combined them with silicone resin emulsion to treat fabrics, a small amount of dosage could make excellent superhydrophobic fabrics. These researches have proved that fluorine-containing finishes have superior oil repellent and antifouling performances and excellent fastness to washing. Even though they are restricted or banned, fluorine-containing finishes are still commonly used in some applications where oil repellent and antifouling properties are highly demanded.

3.1.2 Fluorine-free finishing agent

Despite the common utilization of short-chain fluorine-containing finishing agents, their environmental and human hazards cannot be ignored and the synthesis and application of fluorine-free finishing agents has always been paid attention to. Singh et al.^[23] created

superhydrophobic coating on the surface of cotton fabrics by impregnating them with polytriethoxysilane (PTEVS) and polydimethylsiloxane (PDMS), and photocatalytic activity was achieved by AgBr coating. The water CA of the obtained cotton fabric could reach 154.0° and the sliding angle was 8.0°, indicating good superhydrophobic and self-cleaning properties. Min et al.^[24] prepared a durable antifouling finishing agent based on acrylic polyoxyethylene ether ester, octadecyl methacrylate, acrylic acid and acrylic hydroxyl acrylate through free radical polymerization in the presence of an initiator, and the treated cotton fabric exhibited lasting antifouling effect. Ge et al.^[25] developed a PDMS-in-water emulsion method to design self-healing superhydrophobic cotton fabrics, by which PDMS molecules penetrated and grafted onto cotton fibers to reduce the surface energy of the fabric. The water CA of the treated fabric was more than 155.0° and exhibited excellent chemical stability. Lin et al.^[26] utilized the fluorine-free water repellent agent REPELLAN FF to achieve superhydrophobic cotton fabrics with the REPELLAN FF mass fraction of 8% and drying temperature of 180 °C, which showed CAs of water, isopropanol and glycerol were 150.6°, 146.3° and 152.7°, respectively. Shen et al.^[27] used hydroxyl-terminated polydimethylsiloxane (PDMS-OH), isophorone diisocyanate (IPDI), pentathritol triacrylate (PETA), combining with UV curable coatings to prepare fluorine-free superhydrophobic coating for cotton fabrics, and the water CA was greater than 159.5° with a sliding angle of 7.5°. Additionally, the finished fabrics could maintain superhydrophobic properties even after wear and accelerated washing. Zhang et al.^[28] prepared water repellent and oil repellent cotton fabrics by Daikin fluorine-free waterproof agent XF-5003 TDS and the cross-linking agent PHOBOL® XAN TDS (with the mass concentration of 40 g/L and 15 g/L, respectively) through dip and rolling. The water CA of treated cotton fabric was 119.8° when baking at 140 °C for 3 min, and the wetting area by peanut oil was only 0.055 cm². Generally speaking, the fluorine-free finishing agents can make the fabric better water repellent, but the oil repellent effect is less satisfactory than fluorine-containing finishing agents even with higher dosages.

Silicones contain Si—O—Si bonds, which can make them have low surface energy and good thermal stability, and Si—O—Si bonds can rotate between 105°–180°^[29], so the fabrics after finishing by silicones are relatively soft. Wu et al.^[30] prepared a kind of acrylic acid-silicone mixed resin by modifying polysiloxane with acrylic resin, which endowed cotton fabrics with superhydrophobicity and good abrasion performance. Ou et al.^[31] dipped cotton fabrics into a composite silane solution of hexadecyltrimethoxysilane (HDTMS) and methyl trimethoxysilane (MTMS) to prepare superhydrophobic

cotton fabrics, of which the water CA was 162.5° with repulsive to other daily life liquids such as soy sauce and vinegar. Chauhan et al. [32] treated cotton fabrics with cetyltrimethoxysilane and forcibly immersed the fabric in mud water for 10 min afterward. After being fully cleaned and dried, the fabric showed excellent self-cleaning performance and stain resistance, on which the morphologies of different liquids were nearly spherical. The morphologies of different liquids on the cotton fabric after finishing is shown in Fig. 6 [32]. Lei et al. [33] introduced a trimethylsilicon (M3T) unit into polyacrylate as a functional side chain to make a fluorine-free silicon-based copolymer, which endowed the fabric with good antifouling performance. When the molar fraction of M3T was 72%, the surface energy of the silicon-based copolymer was lowered to 13 mN/m, which was close to that of common fluorine copolymers. The textile treated by this silicon-based copolymer exhibited good antifouling performance against water, juice, red wine and olive oil, droplets of which could stand well on the fabric without wetting it. It is inspired by this research that polymethyl silane monomer may be introduced into other fluorine-free water repellents as a functional side chain, and polymethylene can be used to reduce the surface tension of fabrics, resulting in antifouling and oil repellency effect.



Fig. 6 Different droplet morphologies on cotton fabric after antifouling finishing [32] (Copyright 2019, Elsevier, all right reserved)

In recent years, bio-based materials have attracted more and more attention because of their renewable, green and biodegradable characteristics. In the field of antifouling finishing of textiles, many researchers have also made use of bio-based materials to achieve good results. Liu et al. [34] used a facile strategy to design a bio-based polyurethane (PU) nanofiber membrane with a nanoscale porous structure, which made the membrane have highly waterproof and breathable properties. Zhong et al. [35] used 2-mercaptoethanol with modified castor oil to make a prepolymer, and then prepared a bio-based fluorine-free antifouling coating by using a methylated melamine resin and a curing agent. The coating showed excellent self-cleaning and antifouling performance after many times of friction, and water, crude oil and hexadecane rolled off the coating surface without leaving traces. Therefore, bio-based castor oil can be considered by introducing an organic silicon waterproofing agent into castor oil-based waterborne PU and then finishing the

fabrics to obtain superhydrophobic and antifouling properties.

3.2 Fabrication of homogeneous rough surface with low surface energy

3.2.1 Fabric etching for construction roughness

According to Wenzel model, it has been found that constructing roughness on solid surfaces and then treating the solid surfaces with low surface energy materials can obtain good hydrophobic and antifouling properties, which have been verified for various substrates.

First of all, many researchers have found that etching can produce uniform roughness of the solid surface, which affects the hydrophobicity and oleophobicity of the solid surface. Bhushan et al. [36] studied the wettability of patterned silicon surfaces with cylindrical flat-topped columns of different sizes and spacing, and then covered with hydrophobic phosphorus trifluoride (PF₃) coating. It was found that the wetting behavior of the patterned silicon surfaces depended on the spacing factor (column diameter divided by pitch). The spacing factor controlled the CA, the contact lag angle (CAH) and the sliding angle (SA) of the composite interface area, and the transition from the composite solid-liquid-air interface to the homogeneous solid-liquid interface occurred at the critical value of the spacing factor, independent of the actual size of the roughness and the ratio of the roughness to the droplet size. Zhao et al. [37] created grooves of 3 μm apart (4 μm of height) on a silicon wafer by lithography and then chemically modified the groove surface with a fluorosilane coating. The surface properties were investigated by measuring static CAs and dynamic CAs using water, hexadecane and polyethylene wax inks as probe liquids, and the silicon wafer showed superhydrophobicity. Afterward, a column with a diameter of 3 μm , a height of 7 μm , and a center-to-center spacing of 6 μm was created using the same technique [38]. Then, a fluorosilane coating FOTS was synthesized using molecular vapor deposition technology containing decafluoro-1, 1, 2, 2-tetrahydrooctyltrichlorosilane, exhibiting super repulsion towards water and oil (hexadecane), with CAs of 156.0° and 158.0° for water and hexadecane, respectively. Inspired by the above research, a feasible idea may be provided for the etching of fabrics.

3.2.2 Construction of the reentrant structure

In particular, it was found that the construction of the reentrant structure had a great impact on the matrix's hydrophobicity. Brown et al. [39] impregnated silica nanoparticles with polycarbonate and the reentrant structure existed on the surface of the silica particle aggregated as the nucleation point of polymer crystallization. After being treated with fluorosilane, the matrix's surface showed a high CA and a low SA for water and hexane. Yamaguchi et al. [40] prepared samples with spherical curvature using a UV-curable resin and Teflon microbeads (2.26 μm to 1353.00 μm in

diameter) by spin coating on a glass substrate, and the side view showed that concave textures were formed indeed. The apparent CAs of soy sauce and rapeseed oil on the sample surface with an appropriate bead diameter were 130.2° and 119.4° , respectively. Therefore, the reentrant structure can be constructed on the fabrics, coupled with the treatment of fluorine-free low surface energy materials, resulting in better antifouling fabrics.

In addition to this, Shabanian et al.^[41] developed a technique to prepare oil repellent textiles without PFC agent by adding secondary and smaller-length scale textures on each fiber with a given weave. Excellent oil repellence was achieved when texture size, spacing and surface chemistry were reasonably controlled. For example, the manufactured oil repellent jacket fabric exhibited lipophobic repellence to canola, olive and castor oils in addition to repellence to synthetic sweat, and the fabric remained unwetted for liquid with surface tension as low as 23.9 mN/m.

3.3 Fabrication of non-homogeneous rough surface with low surface energy

With further research on the relationship between matrix surface morphology and water and oil repellence, it has been found that non-homogeneous roughness is more favorable for antifouling of solid surfaces, such as non-homogeneous micro-nano structure on lotus leaf surfaces. Therefore, many researchers constructed non-homogeneous micro-nano structures on the surface of fabrics by different methods, and then low surface energy materials were utilized to obtain good antifouling properties.

3.3.1 Structural roughness of micro-nano structures

To construct roughness on fabric surfaces, silica particles are often used to fabricate micro-nano structures. Wang et al.^[42] doped silica particles in hydrophilic calcium alginate hydrogel to create the coating with layered micro-nano structures. The introduction of nanoparticles significantly reduced the adhesion of oil and improved the mechanical properties of the coating. Due to the hydrophilic and graded micro-nano structures, the prepared coating exhibited excellent oil resistance and self-cleaning properties. Wang et al.^[43] impregnated polyethyleneterephthalate (PET) with hydrophobic SiO_2 nanoparticles and methylphenyl silicone, followed by O_2 plasma treatment and vapor deposition of perfluorooctane trichlorosilane to create a superhydrophobic coating on PET substrate. The obtained PET substrate showed a CA of $153.0^\circ \pm 2.0^\circ$ and a CAH of $4.0^\circ \pm 2.0^\circ$ for hexadecane, indicating good oleophobicity. Yuan et al.^[44] prepared superhydrophobic silica aerogel with porous micro-nano structure on the surface using methyltrimethoxysilane, water and cetyl trimethyl ammonium bromide. Then the silica aerogel powder was coated on the fabric by the spraying method with dimethyl siloxane, and the water CA of the obtained fabric was up to 161.0° , indicating good antifouling properties. Li et al.^[45] treated cotton

fabric with SiO_2 sol, and then He plasma was used to induce 1, 3, 5, 7-tetrasvinyl-1, 3, 5, 7 tetramethylcyclotetrasiloxane (D4Vi) graft polymerizing to coat SiO_2 , obtained hydrophobic and antifouling cotton fabric. Different liquids dripped on the finished cotton fabric without wetting. Lin et al.^[46] prepared a finishing agent containing nano silica and organic fluorine through three steps: preparation of initiator, pre-emulsification and polymerization. Then the finishing agent was coated on the fabric to construct micro-nano structures and the treated fabric obtained good water and oil repellent properties. Gao et al.^[47] used sol-gel method to construct micro-nano structures on the surface of cotton fabric, and then cetyltrimethoxy silane was used for low surface energy modification, achieving a CA of cotton fabric up to 162.0° . Xu et al.^[48] first coated cotton fabric with SiO_2 particles and then used diblock copolymer of poly [(methyl methacrylate)-*b*-(lauryl methacrylate)] (PMMA-*B*-PLMA) to decrease the surface energy, and the obtained cotton fabric possessed a water CA of 156.7° . The studies above show that silica particles have gotten wide application. It is anticipated that the effect of different aggregation forms of silica on the water and oil repellent effect of fabric will be studied in the future.

In addition, silica and other nanoparticles are used to synthesize inorganic-organic nanocomposites that are used as surface treatments to impart good hydrophobicity and antifouling properties to solid surfaces. Feng et al.^[49] prepared inorganic-organic core-shell nanostructured polyester acrylate (PEA)/ SiO_2 emulsion with PEA and vinyl-modified SiO_2 nanoparticles, and the CA of the treated fabric reached more than 151.5° , indicating good hydrophobicity. Yu et al.^[50] synthesized cross-linked amino long-chain alkyl polysiloxanes (CAHPS) by basic equilibrium polymerization, and then prepared chemically bonded organic-inorganic nanohybrid cross-linked polysiloxanes (RSiO_2 -CAHPS) by ring-opening addition reaction with modified nano-silica. The synergistic effect of cotton fiber, nano-silica and low surface energy CAHPS endowed the cotton fabric with a non-homogeneous rough structure, which showed excellent water repellent effect. An et al.^[51] used dodecyl-modified phenyl siloxane resin (PDESr) with amino-functionalized silica nanoparticles (BTEPA- SiO_2) to prepare a novel dodecyl phenyl siloxane (PHDESr- SiO_2) oligomeric resin nanocomposite by graft copolymerization. After impregnation of the cotton fabric, a superhydrophobic structure on the surface of the cotton fabric was constructed with micro and nano nodules, cross-linked network of hydrophobic silicone film and cylindrical dodecyl molecular brush clusters of PHDESr- SiO_2 , resulting in the water CA of the treated fabric up to 152.5° . In future research, nano-silica and other particles grafted onto the fluorine-free finishing macromolecular chain to synthesize the inorganic-organic

composite nano-type antifouling finishing agent may be an effective approach.

3.3.2 Etching of substrate surface

Some researchers etched the substrate surface to increase roughness so that good antifouling performance is obtained. Lee et al.^[52] treated titanium substrate surface by acid etching and anodic oxidation to form hierarchical structures of micro and nano pores, and then coated with a fluorine silane self-assembled monolayer to significantly reduce the surface energy, achieving superhydrophobic and oleophobic properties. By referring to the simple and common method on other substrates, the substrate can be changed into fiber for etching, which provides a good idea for the fluorine-free antifouling finishing of textiles. Cheng et al.^[53] etched silk fabric with papain to produce roughness, and then treated the fabric with methyltrichlorosilane by thermochemical vapor deposition. The obtained fabric showed superhydrophobicity with a water CA up to 156.7° and a SA up to 8.5°. Cheng et al.^[54] etched cotton fabric with cellulase to produce roughness, and then epoxy soybean oil and stearic acid were used to lower surface energy. Superhydrophobic cotton fabric was prepared with a water CA up to 157.0°. Nguyen-Tri et al.^[55] treated the cotton fabric with alkali and plasma etching to obtain uniform roughness. Then the etched fabric was treated with 7 nm silica nanoparticles and a silane water repellent agent ethyl orthosilicate to obtain superhydrophobic property with a water CA as high as 173.0°. It can be seen that it is feasible to construct roughness on the fabric surface by the etching method, and then low surface energy agents are applied to obtain the superhydrophobic and antifouling fabric.

3.3.3 Fabrication of non-homogeneous rough surface with bio-based low surface energy materials

In addition, bio-based materials have been gradually applied in the field of antifouling textiles because of their environmental protection and non-toxic properties. Liu et al.^[56] found that duck feathers had a multi-scale structure, which made the feathers water repellent. Therefore, artificial duck feathers were fabricated on fabrics by a simple solution precipitation method. The microstructure of duck feathers was simulated on the fabric based on chitosan, and then the fabric was further treated with polysiloxane emulsion to obtain lower surface energy. The finished fabric had super water repellent property and a comfortable hand feeling. Cheng et al.^[57] prepared bio-based superhydrophobic and durable cotton fabric by in situ growth-assisted method. The hierarchical structure of the cotton fabric was produced by hydrophobic composite nanoparticle deposition, which was prepared from hydrolysis and condensation of cashew phenol base benzo oxazine (C-aps) and tetraethylorthosilicate (TEOS). The superhydrophobic surface showed a water CA of 158.0°, abrasive wear resistance, acid and alkali liquid

resistance, water droplet impact resistance and excellent durability. Richard et al.^[58] immersed the fabric in a colloidal suspension of zinc hydroxide and then hydrophobized it with stearic acid. The water CA of the finished fabric was 151.0°, indicating that the superhydrophobicity of the fabric was ascribed to the combined effect of the surface roughness given by zinc hydroxide and the low surface energy of stearic acid. Lin et al.^[59] used silica to increase the surface roughness of cotton fabric by sol-gel method, and eleostearic acid (EA) was coated to reduce the surface tension. The EA-SiO₂ coated cotton fabric exhibited excellent superhydrophobicity. Li et al.^[60] prepared flowered MnO₂ nanoparticles on the surface of cotton fabric by in situ growth method and modified it with stearic acid. The water CA of the obtained fabrics was 154.0°, suggesting good hydrophobicity and wear resistance. Kundu et al.^[61] coated amorphous carbon particles onto cotton fabric by plasma-enhanced chemical vapor deposition to achieve hydrophobicity, and then modified with stearic acid to achieve superhydrophobic cotton fabric. Zhang et al.^[62] successfully prepared porous micro and nano fibrous membranes with a large number of nanopores on the fiber surface whose static water CA was up to 145.0°. In the future, it is hoped that more bio-based materials can be developed for antifouling textiles.

3.4 Summary of antifouling finishing methods

To sum up, with the continuous development of antifouling textiles, there are more and more antifouling finishing methods, and the essence is to directly reduce the surface tension of the fabric surface or combine the surface roughness of the fabric with lower surface tension to obtain antifouling properties.

1) From the perspective of reducing the surface tension of fabrics, most researchers are committed to developing fluorine-free antifouling agents, since fluorine-free finishing agents are not toxic and eco-friendly. Silane monomers containing polymethyl groups can be introduced into antifouling agents as functional side chains, and polymethyl groups can reduce the surface tension of the fabric. It is also possible to consider bio-based monomers, for example castor oil, introducing silicone waterproofing agents into castor oil-based waterborne PU, to obtain the effect of water and oil repellent.

2) By combining the surface roughness of the fabric and reducing the surface tension, it is possible to consider micro-etching of the fabric surface, and then coating low surface energy material, so that the fabric can obtain superhydrophobic and antifouling properties. Nano-silica and other particles can also be grafted onto the macromolecular chain of fluorine-free finishing agents to prepare inorganic-organic nanocomposite antifouling finishing agents, which can reduce the surface tension while constructing the surface roughness

of the fabric so that the fabric can obtain good antifouling properties.

4 Summary and Prospect

In this study, CiteSpace and Carrot2 were used to analyze and visualize the relevant literature in the antifouling finishing field in recent years. The theoretical evolution, technical characteristics and research progress of textile antifouling finishing were reviewed. It was shown that based on hydrophobic textiles, fluorine-free antifouling finishing has become a research hotspot. There is an urgent need to develop non-toxic and fluorine-free antifouling agents.

At present, the textile antifouling finishing is developing rapidly, and many methods have been proposed to produce superhydrophobic and antifouling surfaces. Due to the low surface energy of oil, fluorine-containing finishing agents are generally utilized although they have been proven to be harmful to the human body and environment. Thus achieving fluorine-free antifouling finishing has become a difficult problem in the textile industry. In this paper, the three stages of textile antifouling finishing and the popular methods are reviewed, and the future development trend is prospected. Firstly, to reduce the surface energy of fabrics, methyl silane monomers or bio-based monomers can be formulated with other agents to produce antifouling finishing agents. Secondly, constructing the fabric surface roughness while reducing surface tension, micro etching can be utilized to construct roughness, and then using low surface energy materials to reduce surface tension. Thirdly, nanoparticles are utilized to synthesize inorganic-organic nanocomposite antifouling finishing agents, so that the surface tension of fabric can be reduced while forming the roughness, to obtain good antifouling performance.

In this paper, the research progress of textile antifouling finishing is reviewed and future developments are prospected, hoping to provide a reference for researchers in this field. Additionally, to promote the transformation of the industrial sector to fluorine-free, we can strengthen the regulatory restrictions, strengthen the sampling inspection of clothing fabrics and the detection of fluorine in wastewater discharge, and restrict the production of manufacturers.

References

- [1] LI L, WANG S X, LU S Z, et al. The three-proof finishing of real silk (kesi) fabric [J]. *Modern Silk Science and Technology*, 2015, 30: 204-207. (in Chinese)
- [2] ANDRA S, BALU S K, JEEVANANDAM J, et al. Surface cationization of cellulose to enhance durable antibacterial finish in phytosynthesized silver nanoparticle treated cotton fabric [J]. *Cellulose*, 2021, 28(9): 5895-5910.
- [3] HE P S, CHEN X Y, ZHU P, et al. Preparation and flame retardancy of reactive flame retardant for cotton fabric [J]. *Journal of Thermal Analysis and Calorimetry*, 2018, 132(3): 1771-1781.
- [4] YU X, DAI X H, PAN J J, et al. Transesterification reaction and application in anti-wrinkle finishing of cotton fabrics [J]. *Cellulose*, 2021, 28(17): 11183-11197.
- [5] JAVAID S, MAHMOOD A, NASIR H, et al. Layer-by-layer self-assembled dip coating for antifouling functionalized finishing of cotton textile [J]. *Polymers*, 2022, 14(13): 2540.
- [6] YANG Y W. Development of fluorine-free water repellent for textile [J]. *Guangzhou Chemical Industry*, 2020, 48(13): 17-19. (in Chinese)
- [7] ZHAO Qiang, LIU Zhengjiang, MA Huiyan, et al. Application mechanism and research progress of TiO₂ in fabric functional finishing [J]. *Wool Textile Journal*, 2021, 49(9): 102-107. (in Chinese)
- [8] YANG X, HE L C. Status and progress of fluorine-free waterproof finishing agents for textiles [J]. *Printing and Dyeing Auxiliaries*. 2022, 39(5): 11-15. (in Chinese)
- [9] HU J J, LIN S L, YAN J. Research status of fluorine-free waterproofing agents [J]. *Dyeing and Finishing Technology*. 2021, 43(9): 1-4. (in Chinese)
- [10] HONDROS E D. Dr. Thomas Young: natural philosopher [J]. *Journal of Materials Science*, 2005, 40(9): 2119-2123.
- [11] WENZEL R N. Resistance of solid surfaces to wetting by water [J]. *Industrial & Engineering Chemistry*, 1936, 28(8): 988-994.
- [12] ZHAO M Y. Preparation and properties of superhydrophobic coatings containing montmorillonite [D]. Xi'an; Xi'an Polytechnic University, 2018. (in Chinese)
- [13] LEI S, SHI Z Q, OU J F, et al. Durable superhydrophobic cotton fabric for oil/water separation [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2017, 533: 249-254.
- [14] TIAN N, CHEN K, YU H, et al. Super pressure-resistant superhydrophobic fabrics with real self-cleaning performance [J]. *iScience*, 2022, 25(6): 104494.
- [15] ELLINAS K, TSOUGENI K, PETROU P S, et al. Three-dimensional plasma micro-nanotextured cyclo-olefin-polymer surfaces for biomolecule immobilization and environmentally stable superhydrophobic and superoleophobic behavior [J]. *Chemical Engineering Journal*, 2016, 300: 394-403.

- [16] ZHU X H, JIA X H, ZHANG Y Q. The physicochemical and fire extinguishing performance of aqueous film-forming foams based on a class of short-chain fluorinated surfactants [J]. *Journal of Surfactants and Detergents*, 2022, 25(2): 193-204.
- [17] YANG S X. Study on anti-fouling, easy decontamination and antibacterial one-bath finishing process of pure cotton fabric [D]. Shanghai: Donghua University, 2019. (in Chinese)
- [18] DONG L, SHI M, XU S J, et al. Surface construction of fluorinated TiO₂ nanotube networks to develop uvioresistant superhydrophobic aramid fabric [J]. *RSC Advances*, 2020, 10(38): 22578-22585.
- [19] QIAN H H, DU J M, FU J J, et al. Synthesis and application of water and oil repellent finishing agent with short chain fluoroacrylate [J]. *Polymer Materials Science & Engineering*, 2019, 35(2): 22-28.
- [20] LI G, ZHENG H T, WANG Y X, et al. A facile strategy for the fabrication of highly stable superhydrophobic cotton fabric using amphiphilic fluorinated triblock azide copolymers [J]. *Polymer*, 2010, 51(9): 1940-1946.
- [21] LI Y T, HOU Q Q, FENG H B, et al. Synthesis and application of short-chain perfluoroacrylate emulsion [J]. *China Dyeing & Finishing*, 2014, 40(21): 27-29. (in Chinese)
- [22] GOU W W, CHE X G, YU X J, et al. Facile fabrication of waterborne fabric coatings with multifunctional superhydrophobicity and thermal insulation [J]. *Materials Letters*, 2019, 250: 123-126.
- [23] SINGH A K, SINGH J K. Fabrication of durable superhydrophobic coatings on cotton fabrics with photocatalytic activity by fluorine-free chemical modification for dual-functional water purification [J]. *New Journal of Chemistry*, 2017, 41(11): 4618-4628.
- [24] MIN J, JIANG S S, HU X C, et al. Synthesis and application of textile functional finishing polymer with durability and easy decontamination: CN202010365987.2 [P]. 2020-07-03.
- [25] GE M Z, CAO C Y, LIANG F H, et al. A "PDMS-in-water" emulsion enables mechanochemically robust superhydrophobic surfaces with self-healing nature [J]. *Nanoscale Horizons*, 2020, 5(1): 65-73.
- [26] LIN X H, LI S S, MU T, et al. Preparation and application of fluorine-free superhydrophobic cotton fabric [J]. *China Dyeing & Finishing*, 2018, 44(17): 5-10. (in Chinese)
- [27] SHEN L X, PAN Y, FU H Q. Fabrication of UV curable coating for super hydrophobic cotton fabrics [J]. *Polymer Engineering & Science*, 2019, 59(2): 452-459.
- [28] ZHANG L, MENG J G. Optimization of water-repellent and oil-repellent finishing process of pure cotton fabric [J]. *Journal of Zhejiang Textile and Apparel Vocational College*, 2021, 20(3): 9-14. (in Chinese)
- [29] ZHOU P F, YAO A K, WANG S F, et al. Application of organosilicon in water-repellent finishing of textiles [J]. *Applied Chemical Industry*, 2021, 50(4): 1031-1036. (in Chinese)
- [30] WU J M, HU Z W, LU W G, et al. Fabricating self-stratifying coating for superhydrophobic cotton textile [J]. *Journal of Applied Polymer Science*, 2022, 139(17): 1-9.
- [31] OU J F, WANG F J, LI W, et al. Methyltrimethoxysilane as a multipurpose chemical for durable superhydrophobic cotton fabric [J]. *Progress in Organic Coatings*, 2020, 146: 105700.
- [32] CHAUHAN P, KUMAR A, BHUSHAN B. Self-cleaning, stain-resistant and anti-bacterial superhydrophobic cotton fabric prepared by simple immersion technique [J]. *Journal of Colloid and Interface Science*, 2019, 535: 66-74.
- [33] LEI H, XIONG M N, XIAO J, et al. Fluorine-free low surface energy organic coating for anti-stain applications [J]. *Progress in Organic Coatings*, 2017, 103: 182-192.
- [34] LIU H K, WANG T, YAN Z S et al. Elastic bio-based polyurethane nanofibrous membrane with robust waterproof and breathable properties [J]. *Journal of Donghua University (English Edition)*, 2023, 40(3): 237-246.
- [35] ZHONG X M. Preparation, properties and application of fluorine-free anti-fouling coatings [D]. Guangzhou: South China University of Technology 2020. (in Chinese)
- [36] BHUSHAN B, NOSONOVSKY M, JUNG Y C. Towards optimization of patterned superhydrophobic surfaces [J]. *Journal of the Royal Society Interface*, 2007, 4(15): 643-648.
- [37] ZHAO H, LAW K Y. Directional self-cleaning superoleophobic surface [J]. *Langmuir: the ACS Journal of Surfaces and Colloids*, 2012, 28(32): 11812-11818.
- [38] ZHAO H, LAW K Y, SAMBHY V. Fabrication, surface properties, and origin of superoleophobicity for a model textured surface [J]. *Langmuir: the ACS Journal of Surfaces and Colloids*, 2011, 27(10): 5927-5935.
- [39] BROWN P S, BHUSHAN B. Durable, superoleophobic polymer-nanoparticle composite

- surfaces with re-entrant geometry via solvent-induced phase transformation [J]. *Scientific Reports*, 2016, 6: 21048.
- [40] YAMAGUCHI M. Microfabrication of re-entrant surface with hydrophobicity/oleophobicity for liquid foods [J]. *Scientific Reports*, 2020, 10: 2250.
- [41] SHABANIAN S, KHATIR B, NISAR A, et al. Rational design of perfluorocarbon-free oleophobic textiles [J]. *Nature Sustainability*, 2020, 3: 1059-1066.
- [42] WANG C Q, ZHANG F L, YU C M, et al. Durable underwater superoleophobic coatings via dispersed micro particle-induced hierarchical structures inspired by pomfret skin [J]. *ACS Applied Materials & Interfaces*, 2020, 12(37): 42430-42436.
- [43] WANG Y X, BHUSHAN B. Wear-resistant and antimudge superoleophobic coating on polyethylene terephthalate substrate using SiO₂ nanoparticles [J]. *ACS Applied Materials & Interfaces*, 2015, 7(1): 743-755.
- [44] YUAN X L, XU L H, WAN J, et al. Preparation of fluorine-free self-cleaning superhydrophobic cotton fabric based on hydrophobic silica aerogel [J]. *China Dyeing & Finishing*, 2021, 47(2): 40-44. (in Chinese)
- [45] LI Y Q, ZOU C, SHAO J Z, et al. Fabrication of superhydrophobic cotton fabrics through wrapping silica with plasma-induced grafting polymerization [J]. *Textile Research Journal*, 2019, 89(3): 401-410.
- [46] LIN C X, LIU D H, LUO W, et al. A core-shell fabric finishing agent containing fluorine and silicon and its preparation method: CN201410115953[P]. 2014-07-23.
- [47] GAO J, LIU J, XU R F, et al. Micro-nanostructure-based super-hydrophobic surface on cotton fabric [J]. *Textile Research Journal*, 2018, 88(22): 2602-2610.
- [48] XU Q B, WANG L J, FU F Y, et al. Fabrication of fluorine-free superhydrophobic cotton fabric using fumed silica and diblock copolymer via mist modification [J]. *Progress in Organic Coatings*, 2020, 148: 105884.
- [49] FENG Q, WANG X L, ZHOU Q F. PEA/V-SiO₂ core-shell structure for superhydrophobic surface with high abrasion performance [J]. *Surfaces and Interfaces*, 2018, 12: 196-201.
- [50] YU C B, SHI K Q, NING J Y, et al. Preparation and application of fluorine-free finishing agent with excellent water repellency for cotton fabric [J]. *Polymers*, 2021, 13(17): 2980.
- [51] AN Q F, PAN J Y, ZHANG B, et al. Synthesis of a dodecylphenylsiloxane oligomer resin/silica nanocomposite and its application to cotton fabrics [J]. *Fibers and Polymers*, 2016, 17(7): 1069-1077.
- [52] LEE J W, HWANG W. Simple fabrication of superoleophobic titanium surfaces via hierarchical microhorn/nanoporous structure growth by chemical acid etching and anodization [J]. *Journal of Alloys and Compounds*, 2017, 728: 966-970.
- [53] CHENG Y, ZHU T X, LI S H, et al. A novel strategy for fabricating robust superhydrophobic fabrics by environmentally-friendly enzyme etching [J]. *Chemical Engineering Journal*, 2019, 355: 290-298.
- [54] CHENG Q Y, ZHAO X L, WENG Y X, et al. Fully sustainable, nanoparticle-free, fluorine-free, and robust superhydrophobic cotton fabric fabricated via an eco-friendly method for efficient oil/water separation [J]. *ACS Sustainable Chemistry & Engineering*, 2019, 7(18): 15696-15705.
- [55] NGUYEN-TRI P, ALTIPARMAK F, NGUYEN N, et al. Robust superhydrophobic cotton fibers prepared by simple dip-coating approach using chemical and plasma-etching pretreatments [J]. *ACS Omega*, 2019, 4(4): 7829-7837.
- [56] LIU Y Y, CHEN X Q, XIN J H. Hydrophobic duck feathers and their simulation on textile substrates for water repellent treatment [J]. *Bioinspiration & Biomimetics*, 2008, 3(4): 046007.
- [57] CHENG J W, SHANG Q Q, LIU C G, et al. Fabrication of cardanol-based superhydrophobic cotton fabric for highly effective oil-water separation [J]. *Materials Today Communications*, 2021, 29: 102820.
- [58] RICHARD E, LAKSHMI R V, ARUNA S T, et al. A simple cost-effective and eco-friendly wet chemical process for the fabrication of superhydrophobic cotton fabrics [J]. *Applied Surface Science*, 2013, 277: 302-309.
- [59] LIN H M, CHEN K H, ZHENG S J, et al. Facile fabrication of natural superhydrophobic eleostearic acid-SiO₂@cotton fabric for efficient separation of oil/water mixtures and emulsions [J]. *Sustainable Materials and Technologies*, 2022, 32: e00418.
- [60] LI D K, GUO Z G. Stable and self-healing superhydrophobic MnO₂@fabrics: applications in self-cleaning, oil/water separation and wear resistance [J]. *Journal of Colloid and Interface Science*, 2017, 503: 124-130.
- [61] KUNDU D, BANERJEE D, GHOSH S, et al. Plasma enhanced Chemical Vapour deposited amorphous carbon coating for hydrophobicity enhancement in commercial cotton fabrics [J]. *Physica E: Low-Dimensional Systems and*

Nanostructures, 2019, 114: 113594.

- [62] ZHANG X X, SU Y Z, SHI L X, et al.
Preparation of cellulose acetate butyrate porous

micro/nanofibrous membranes and their properties [J]. *Journal of Donghua University (English Edition)*, 2023, 40(5):461-466.

纺织品防污整理综述：主题、演进与方法

丁凤美^{1,2}, 郭亚丽^{1,2}, 王庆森³, 王雪慧^{1,2}, 王平³, 邢志奇¹, 陈璐怡^{4*}

1. 东华大学 化学与化工学院, 上海 201620
2. 东华大学 国家染整工程技术研究中心, 上海 201620
3. 雅戈尔集团股份有限公司, 浙江 宁波 315153
4. 上海市国资国企改革研究中心, 上海 200233

摘要：防污纺织品是近十年来研究的热点。欧洲计划从 2025 年起禁止生产 C6 含氟三防（防水、防油、防污）整理剂，实现完全无氟防污。该综述结合三防领域现行无氟处理政策规定，进行文献调查、分析和总结，了解无氟防污整理的研究现状和趋势。采用 CiteSpace 和 Carrot2 对 Web of Science 和 CNKI 两个数据库中的最新论文进行文献综述研究。首先，系统讨论了纺织品防污整理的理论演进和技术特点，并比较了不同需求的防污整理纺织品的技术差异。其次，总结了纺织品防污整理发展的三个主要阶段及其相应的整理方法。最后，展望了无氟防污整理未来发展的三条路径：低表面能结构、均匀粗糙低表面能结构、多级粗糙低表面能结构。为促进工业领域的生产和使用向无氟转型，应加强监管限制，加强对服装面料的抽样检查，检测废水排放中的氟，并限制制造商生产含氟整理剂。

关键词：防污整理；无氟；疏水性；疏油性；表面粗糙度