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EDITORIAL

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Pickering aqueous foam templating: a promising strategy to fabricate porous waterborne polyurethane coatings

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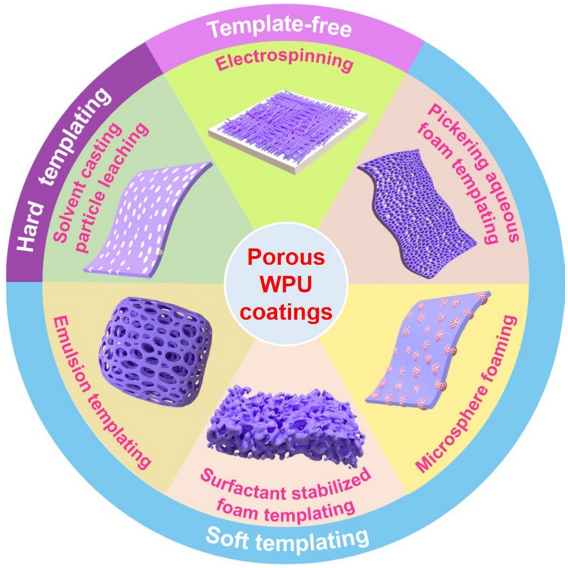
Graphical abstract



Waterborne polyurethane (WPU) has been widely used as coatings in industrial fields ranging from wood, real/synthetic leather, and textiles, because it exhibits versatile performance, excellent eco-friendliness, and superior film-forming property. In terms of wearable products, compact WPU coatings often cause discomfort due to the intrinsic poor vapor transmission. Moreover, the resultant relatively high humidity promotes the growth of skin flora, resulting in unpleasant odors, and even skin infectious diseases. To this end, breathable porous WPU coatings with tunable pore size has emerged as a favorable alternative to modulate the "climate" of

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microenvironment at the interface between skins and wearable products. Several strategies have been now developed to engineer porous WPU coatings. In this perspective, we describe various strategies that have been developed to manufacture porous WPU coatings. According to whether the template is used and the category of templates used, we categorize these strategies into three different types, including hard templating, soft templating, and template-free methods. We discuss the advantages and disadvantages of each strategy and highlight the importance in developing new strategies of making highly breathable WPU to help the sustainable growth of the leather industry.

1 Hard templating

Figure 1 illustrates the different approaches to produce porous WPU coatings. Hard templating, which is also called as solvent casting particle leaching, has been widely used to fabricate multiple porous polymer, including WPU [1]. In the strategy, solid particles are used as templates to pre-occupy the voids of the WPU matrix, and subsequently dissolved/leached out from matrix to obtain porous WPU coatings. Specifically, solid particles with defined size (e.g., calcium carbonate) are added into WPU dispersion; after evaporation of the medium, particles are embedded throughout WPU matrix. Finally, these particles are removed by dissolving and/or etching, leaving porous structures. The method shows uniform cell sizes and facile production. However, it is challenging to maintain adequate mechanical property and produce a thick coating, since such particles are not easily to leach out in a bulky volume. Besides, organic solvents are necessitated to remove the template cores, which raise the health and environment-related issues. Meanwhile, the poor pore connectivity (i.e., closed pores) is unfavourable to the vapor transmission.

2 Soft templating

The templates used in soft-templating methods are typically liquid or gas. On the basis of its types, soft templating involves emulsion templating and foam templating.

Emulsion templating requires the emulsification of two immiscible liquid phases, where the dispersed phase contains organic solvent and the continuous phase contains the WPU-rich water. The emulsion is quickly

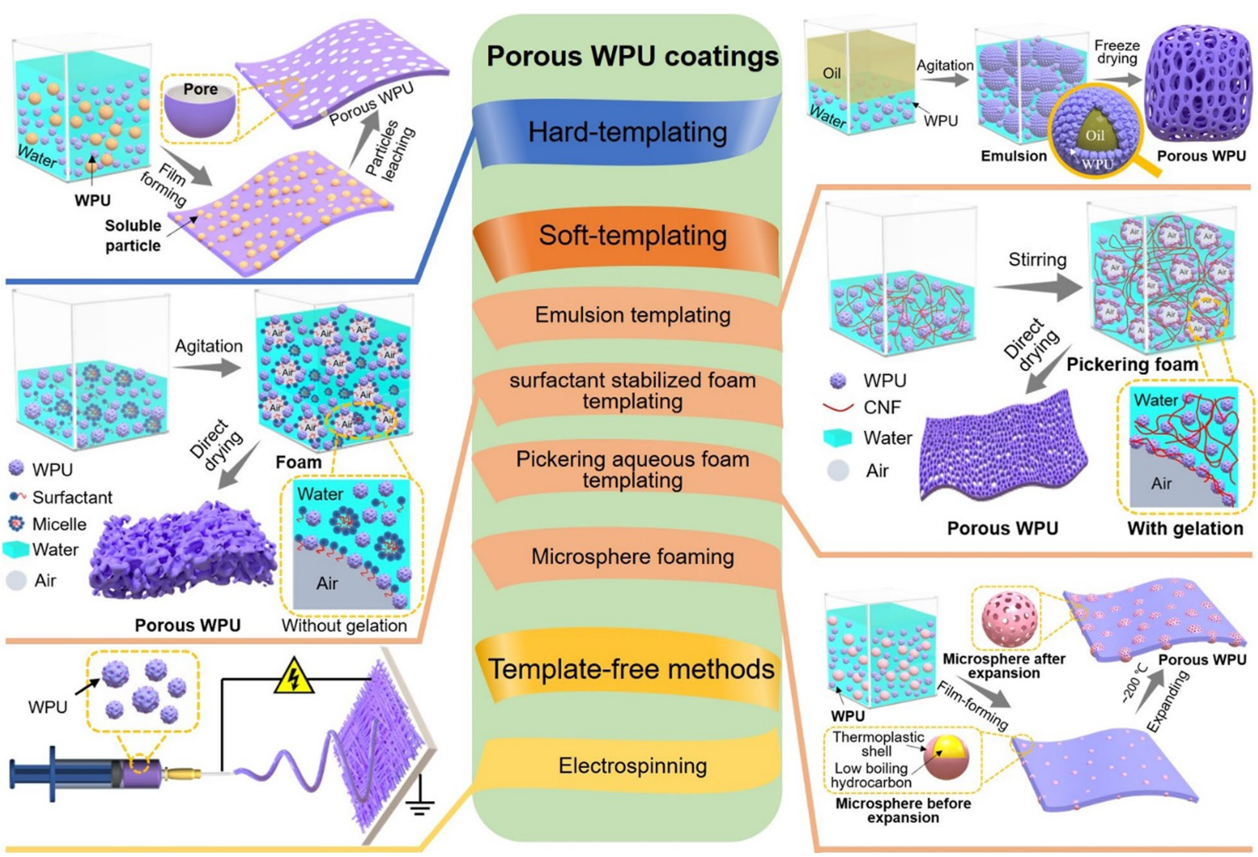

Fig. 1 Schematic illustration of the fabrication techniques for porous WPU coatings

frozen to maintain its structure, and is then freeze-dried to manufacture a porous WPU, exhibiting great flexibility in tailoring the morphology of the product and its corresponding breathability and mechanical property [2]. The main disadvantage is the removal of the dispersed phase, which makes this method environmental unfriendly and economically uncompetitive.

Foam templating can be classified as surfactant stabilized foam templating and microsphere foaming based on the formation mechanism of the foam. The former has been proposed as a very effective way of fabricating porous WPU coatings because of its simple, solvent-free, and easy scale-up production. This technique entails the introduction of air into high-viscosity WPU dispersion (> 45 wt%) to form wet foams, followed by direct drying under high temperature. Surfactant is often used to stabilize the foams during preparation and drying [3]. However, such wet foams commonly have poor long-term stability due to molecular surfactant, whose desorption energy is comparable to thermal energy, and constantly adsorb and desorb from the air-liquid interface leading to the drainage effects under gravity, which in turn causes uncontrolled pore structure and size.

Microsphere foaming involves the expansion of thermally expandable microspheres (TEMs) in the WPU matrix. TEMs are 10–50 μm particles with core–shell structures, which are composed of a thermoplastic shell (e.g., polyacrylonitrile) encapsulated with an inert low boiling hydrocarbon (e.g., *i*-pentane). Upon the temperature reaches up to the glass transition temperature (T_g) of the polymeric shell and the boiling point of the hydrocarbon, microsphere expand 40–60 times in volume due to the large internal pressure caused by an encapsulated volatile hydrocarbon [4]. The formation of uniform pores does not require any additional preprocess or postprocess steps. However, the microspheres are relatively expensive, and the presence of microspheres will adversely affect the properties of WPU porous coatings. Moreover, the volatile organic compounds (VOCs) produced by low boiling organic solvent greatly limit its application.

3 Template-free method

In addition to the template-involved strategies, electrospinning has also been used to produce porous WPU coatings by random stacking of nano- and micro-scale fibers. In brief, a jet of WPU dispersion is ejected from a spinneret when the electrical potential overcomes the surface tension. Interconnected non-woven web is then obtained on the collector after evaporating the water [5]. However, to transfer electrospinning method from laboratory to industrial production, there still exist many challenges such as the clogging of the spinneret, precisely controlling the morphology of the fibers, and poor fiber distribution in the collected mat. WPU dispersion must be above a critical concentration to prepare smooth fibers without any bead appearance and operated under suitable process parameters including applied electrical potential, dispersion flow rate and spinneret-to-collector distance. Besides, the high voltage in electrospinning process may cause danger to the workers.

4 Pickering aqueous foam templating

In recent years, the aqueous foams stabilized by solid particles (i.e., Pickering aqueous foam) have emerged as an ideal template to fabricate porous materials and show great application potential in various fields. Compared to surfactant-stabilized counterparts, particle-stabilized air bubbles are less susceptible to coalescence and Ostwald ripening, because once the particle is adsorbed at the air-water interface it is effectively trapped there so particle attachment is irreversible. By adjusting the processing parameters including air volume fraction, particle properties (e.g., wettability, size, and species), frothing and drying conditions, controllable pore architecture (e.g., pore size, pore connectivity and distribution) can be obtained for versatile porous materials with tunable breathability and mechanical properties. Collectively, this method exhibits various advantages such as outstanding long-term stability, eco-friendly processing, controlled pore structures and thus the properties of porous materials.

However, despite the demonstrable practical usefulness of Pickering foams, liquid films will become thinner and finally rupture as the liquid drainage from the continuous phase of foam, which eventually lead to the foam disappearance and pore structure collapses. To ensure the high-fidelity pore structures, the continuous phase can be solidified by polymerization and gelation. In these systems, polymerization in continuous phase is merely suitable for water-soluble monomers such as acrylamide, which is not interfering the synthesis of WPU. Alternatively, gelation in continuous phase can be achieved by using high aspect ratio particles, and then the solidified aqueous foam is dried directly under high temperature, producing porous materials without structure collapses [6]. For example, cellulose nanofibrils (CNFs) with width in the nanometer range and length up to microns, can form intertwined network in continuous phase at a low concentration (i.e., 5 g/L) [7]. Most importantly, they have been proven to act synergistically with other particles (e.g., silica) to stabilize aqueous foam [8]. Considering WPU particles also exhibit high interface activity and can bind to CNFs through hydrogen bonding, it should be possible to create aqueous foam with high stability and solidified continuous phase via the synergistic effects from WPU and CNFs. In production, the solidified aqueous foam is coated on the surface of non-woven or fabrics, followed by direct drying under high temperature, and then a porous WPU coating can be obtained.

In summary, this paper overviews the methods used to fabricate porous WPU coatings as well as their characteristics. We envision that the Pickering aqueous foam template technique has several advantages among existing methods, including controlled pore structure and size, simple procedures, and low cost, which may provide a convenient pathway for producing porous WPU coating for potential applications.

Abbreviations

WPU	Waterborne polyurethane
TEMs	Thermally expandable microspheres
VOCs	Volatile organic compounds
CNFs	Cellulose nanofibrils

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Author contributions
JW wrote the original draft. JZ and TN revised the written draft. ZS summarized the references and revised Figure. CW and WL and proposed the scientific idea and designed the outline of the draft, and supervised the project. All authors read and approved the final manuscript.

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Declarations

Competing interests
The authors declare that they have no competing interests.

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