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Fish-Mimicking Hydrophilic and Hygroscopic Transparent Films with Long-Lasting Anti-Oil Adhesion and Its Application to PET Bottles

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Abstract: With the recent ban on the production and use of long-chain perfluorinated compounds, the development of alternative approaches to prepare liquid-repellent surfaces that avoids the use of such compounds has become an urgent issue. We have succeeded in the development of fish-mimicking hydrophilic transparent hydrogel-based films with long-lasting anti-oil adhesion properties. Such films could be prepared by simply mixing poly(vinylpyrrolidone) (PVP), nanoclay particles (NCPs), and a waterborne aminosilane (AOS) using an integral blend (IB) method. When submerged in water, these films displayed underwater superoleophobicity (advancing and receding contact angles (CAs) of diiodomethane were $\sim 171^\circ / \sim 163^\circ$) with low CA hysteresis (less than 8°), because the hydrophilic nature of the films promoted the formation of a thin layer of adsorbed water on the topmost film surfaces, similar to fish scales. Furthermore, when our films were coated onto the inside of poly(ethylene terephthalate) (PET) bottles and pre-wetted using 80°C hot water vapors, these film surfaces could effectively repel various oils and were able to maintain their oil-repellent properties for more than 5 weeks. These water-driven, non-perfluorinated transparent hydrogel-based films are expected to increase recycling of PET bottles for oils that are generally incinerated or landfilled.

Keywords: anti-oil adhesion; underwater superoleophobicity; recycling of PET bottles; hydrophilic properties; fish-mimicking; antifogging



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1. Introduction

The use of superhydrophobic/superoleophobic surfaces (hereafter described as super liquid-repellent surfaces) with an extremely high (exceeding 150°) static contact angle (CA, θ_s) for aqueous/organic liquids have attracted much attention over the past few decades for a wide variety of practical applications, including lubrication, self-cleaning, anti-corrosion, and poly(ethylene terephthalate) (PET) recycling [1–5]. Such super liquid-repellent surfaces are generally prepared through combining micro/nano-textured surfaces with surface modifications using lower surface energy materials, often employing long-chain perfluorinated compounds for preparing the latter surfaces [2,4,6–8]. Although these approaches are very promising for designing and preparing potentially useful super liquid-repellent surfaces, formation of such surfaces with intricate textures and 3D nano- and microstructures generally requires complicated and time-consuming surface roughening techniques consisting of many processes, which may be very challenging and expensive to scale-up.

Furthermore, due to concerns about the accumulation of long-chain perfluorinated compounds, especially perfluorooctanoic acid (PFOA), in the human body and the environment, the production and use of PFOA, its salts, and PFOA-related substances were prohibited in 2019 [9,10]. Additionally, due to growing concerns of microplastics and the leaching of chemicals into the plastic, the recycling of various plastics is a complex issue [11–14]. Because of these human, environmental, and regulatory concerns, plastics

from non-food sources are generally incinerated for power generation or otherwise disposed of in landfills [11–14]. PET is one of the most recycled plastics due to its low level of additives (6–25%) used in its formulations [12–15]. Yet, other organic contaminants hamper its recyclability [12–15]. As such, preventing the adsorption of oils and other contaminants using non-permanent coatings should help improve the overall recyclability of PET. Therefore, the development of alternative oil-repelling materials and surface treatments that do not rely on harmful perfluorinated compounds has become an urgent issue for both human and environmental health.

In contrast to such super liquid-repellent surfaces, highly hydrophilic/superhydrophilic surfaces (water θ_S of $<5^\circ$ to $<40^\circ$) can be prepared without relying on surface micro/nano-textures or perfluorinated compounds [16]. Highly hydrophilic/superhydrophilic surfaces can be prepared on a variety of materials through several approaches, including the activation of the surfaces (either through chemical or UV/plasma treatments) [17], highly water-absorbent polymers [18,19], ionic polymer brushes/monolayers [20], hydrogel-based films [21–23], hygroscopic silica (SiO_2), and/or photocatalytic TiO_2/ZnO films [24–26]. These surfaces are generally smooth and flat, so the design of the substrates used are not affected by the surface morphologies. Thus, highly hydrophilic/superhydrophilic surfaces have been developed and widely applied as treatments for transparent objects for the purpose of sustaining visual clarity for windows, lenses, mirrors, and components for medical and scientific equipment [19]. Some highly hydrophilic/superhydrophilic surfaces have taken inspiration from fish scales to gain another advantage in that they display superoleophobicity when submerged in water due to the formation of a thin layer of adsorbed water across the surface [27]. Some of the authors previously developed hydrogel-based superhydrophilic films consisting of polyvinylpyrrolidone (PVP) and amino-functionalized nano-clay particles (NCPs) that display such underwater superoleophobicity among various other properties including antifogging, antibacterial, and self-healing properties [21–23]. However, these films lacked sufficient stability in water and would dissolve almost immediately when submerged in water [21,23], which has been similarly observed for other gel-based films. It is well known that increasing the cross-linking density usually improves underwater stability, but at the expense of other film properties including transparency, hydrophilic and antifogging properties and so on. Therefore, the creation of (super)hydrophilic hydrogel-based films that show underwater stability without sacrificing other film properties is still very challenging.

In this study, we have particularly focused on improving the water stability of these hydrogel-based films on glass slides, Si wafers, and PET substrates to better resist bulk water. These films were prepared by simply mixing PVP, NCPs, and waterborne amino-terminated organosilane (AOS) based on an integral blend (IB) method [28,29]. By increasing the AOS concentration, the stability against bulk water was improved. When submerged in water, these films (hereafter referred to as PVP/NCP/AOS films) displayed superoleophobicity and good oil-repellent properties, with advancing (θ_A) and receding (θ_R) CAs of $\sim 171^\circ$ and $\sim 163^\circ$ and low CA hysteresis (less than 8°) for diiodomethane (DIM) in water. When coated onto the inside of PET bottles and pre-wetted with 80°C hot water vapors, these film surfaces formed a stable and long-lasting water-thin layer like fish scales, with oil-repellent properties lasting for more than 5 weeks. These water-driven, non-perfluorinated hydrophilic transparent films showing superoleophobicity in water and anti-oil adhesion properties at the oil/film interface are completely environmentally friendly and are expected to greatly help and increase recycling of PET bottles that would otherwise be incinerated or landfilled.

2. Materials and Methods

2.1. Materials

PVP (molecular weight: 55 k) was purchased from Sigma-Aldrich. Synthetic NCPs (LAPONITE RD, $[\text{Mg}_{5.34}\text{Li}_{0.66}\text{Si}_8\text{O}_{20}(\text{OH})_4]\text{Na}_{0.66}$, layered silicate clay with an average thickness of 0.92 nm and an average diameter of 25 nm) were purchased from BYK-Chemie

GmbH (Wesel, Germany). AOS aqueous solution (KBP-90; solid content of 30 weight (wt)%) and silicone oil (KF-96-10CS; T11) was purchased from Shin-Etsu Chemical Co., Ltd., Tokyo, Japan. Octane was purchased from Fujifilm Wako Corporation, Osaka, Japan. Vegetable and Canola oil were purchased from local markets. DIM was purchased from Tokyo Chemicals Industry Co., LTD., Osaka, Japan. PET sheets (50 μm thick, 5 cm by 200 m) and PET bottles (100 mL) were purchased from AS ONE Corp, Osaka, Japan. Deionized (DI) and filtered water was used for all sample preparation and CA measurements. All chemicals were used as received without further purification.

2.2. Preparation of PVP/NCP/AOS-Based Hydrogel Films

First, 2.5 wt% solutions of NCPs were created by dispersing 1 g of NCPs in 39 g of H_2O (total weight of 40 g). The mixture was then allowed to mix for 20 min under magnetic stirring until a transparent solution was obtained. Four grams of PVP was then added to this transparent solution and placed in an 80 $^\circ\text{C}$ oven for 3 h to dissolve the PVP. Once the PVP was dissolved, the AOS was added from a diluted solution of AOS (10 wt% solution of AOS). The PVP/NCP/AOS precursor solution was then homogenized using an ultrasonic homogenizer (LUH300, Yamato Scientific Co., Ltd., Tokyo, Japan) for 3 min to obtain a translucent precursor solution at the specified $\alpha\%$ (0–5 $\alpha\%$), where α denotes the weight ratio of AOS to PVP. After homogenization, the solutions were then spin-casted in 2 stages (1000 rpm for 5 s and 2000 rpm for 10 s) onto vacuum-UV (VUV)-oxidized glass slides, Si wafers (10^3 Pa for 10 min), and PET sheets (10^3 Pa for 20 min). PET bottles were also VUV-oxidized (10^3 Pa for 60 min), and approximately 2 mL of precursor solution was added to the bottle. The bottle was then slowly rotated in order to ensure the precursor solution entirely coated the inner surface. After the surface was coated, any excess liquid was removed by gravity. After casting, these samples were cured at 80 $^\circ\text{C}$ for 1 h on glass slides or Si wafers and at 60 $^\circ\text{C}$ for 3 h for PET substrates in order to promote cross-linking.

To obtain a thin layer of adsorbed water on the topmost film surfaces, the samples were exposed to 80 $^\circ\text{C}$ hot water vapors in advance in order to successfully saturate the surface. For the films on PET sheets and PET bottles, 1 min and 10 or 20 min of exposure, respectively, was used in order to ensure that water was adsorbed throughout the films.

2.3. Measurements

For characterization of the coated surfaces, we used an optical microscope (VHX-8000, Keyence, Osaka, Japan). Film thickness measurements were performed using a confocal microscope (OPTELICS HYBRID, Lasertec Corporation, Yokohama, Japan). CAs were measured using a DropMaster DM-501 (Kyowa Interface Science Co., Ltd., Saitama, Japan) and the software FAMAS version 3.7.2. For the water θ_s measurements in air, a 3 μL droplet was placed onto the surface and allowed to equilibrate for 10 s. For the underwater static/dynamic CA measurements, a 3 μL droplet of DIM was gently placed onto the surface (for θ_s measurements), and then DIM was slowly added or removed from the droplet to measure θ_A and θ_R values, respectively. The α value was measured using a 3 μL droplet of DIM and slowly tilting the sample stage ($\sim 1^\circ/4$ s). The final static/dynamic CAs were determined by taking mean values of 3 different points.

Optical transparency of the samples on glass slides in the visible wavelength range was measured using a UV-vis spectrometer (Model U4100, Hitachi High Technologies Corp., Tokyo, Japan). Atomic force microscopy measurements were conducted on an XE-100 AFM, (Park Systems, Suwon, Republic of Korea) in noncontact mode with a Si cantilever (Park Systems, 910MNCHR; spring constant = 42 N/m and response frequency of 330 kHz). Antifogging tests were performed by keeping the coated samples approximately 2 cm above 80 $^\circ\text{C}$ water for 1 min, and then images were captured using a digital camera (iPhone 3) above a checkered background.

For the oil adsorption tests, a PET sheet (5 cm $\times$ 5 cm) was coated with the 5- $\alpha\%$ precursor solution following the above procedure. Some of the coated samples were subjected to pre-wetting to generate a thin layer of adsorbed water on the topmost film

surface by exposing the films to 80 °C hot water vapors for 1 min. These films were then partially immersed (~1.5 cm) in various dyed oils and then removed to see how much oil adhered to the surfaces. The non-coated sides of the substrates were carefully wiped with hexane in order to remove excess oil before any images were captured. When testing the durability of the oil-repellent properties, the coated PET bottles were pre-wetted using 80 °C hot water vapors for 10 or 20 min and then filled with approximately 10 mL of dyed canola oil. The oil was then applied to the entire inner surface of the PET bottles and then allowed to drip down via gravitational forces. For comparison, an uncoated PET bottle was subjected to the same VUV oxidation procedure.

3. Results and Discussion

The major drawback of our previous hydrogel-based films was that the films easily dissolved in bulk water [21]. In our earlier research using the IB method [23], the AOS content was limited to 1 α% in order to obtain transparent films. These films lacked sufficient stability against bulk water and could be easily removed from various substrates when wetted. Therefore, we expected that if we could increase the AOS content, we could increase the cross-linking density by increasing non-covalent (hydrogen bonding and electrostatic) interactions. This increase in the cross-linking density effectively stiffens the polymer chains, making it harder for them to swell in a solvent (e.g., water) [30]. When using the alternative mixing method in this study, there was better dissolution of PVP, NCPs, and AOS; inhomogeneity within the PVP/NCP/AOS precursor solution was not observed even when the AOS content was substantially increased up to 100 α%. However, above 10 α%, the as-casted films began to display several noteworthy instabilities, such as inhomogeneous coverage and radial instabilities. Therefore, in this study, we kept the α content at less than or equal to 5%.

The average thickness of the resulting films was in the range of 700–900 nm. As shown in Figure 1A, this typical AFM image revealed a fairly smooth surface at short length scales (3 μm × 3 μm). The average root-mean-square roughness (R_{rms}) of the sample surface was estimated to be about 3 nm from the AFM image. Furthermore, these films showed high transparency with >90% transmittance at 550 nm (Figure 1B). Therefore, there were no significant deviations from our previous reports on related hydrogel-based films [21–23], even though AOS was increased up to 5 α%.

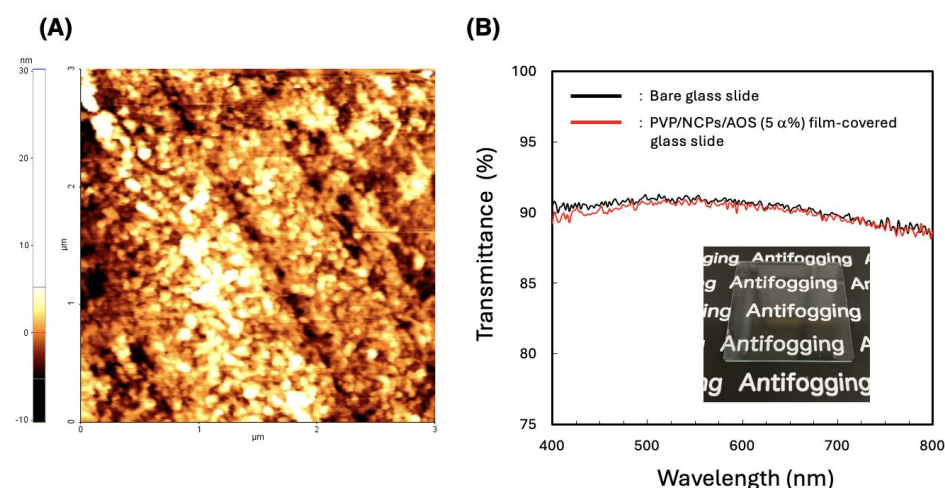


Figure 1. (A) Characteristic AFM image of PVP/NCP/AOS (5 α%) film. Image is a 3 μm × 3 μm area of a film coated Si wafer. Measured root-mean-square roughness was 2.6 nm (B) UV-vis spectra of the glass slides (4 cm × 4 cm) covered with and without PVP/NCP/AOS (5 α%) film and an optical image of the sample.

One potential concern was that increasing the α% content would impact the hydrophilicity of the films. However, water θ_s measurements showed no significant deviation

(max 7°) from our previously optimized films (1 $\alpha\%$, θ_s of 17°) [21–23], indicating that the increased AOS content did not impact the hydrophilicity of the PVP/NCP/AOS films. We did expect that the increased cross-linking density would improve the water stability of these films, because of the increased amount of hydrogen bonds from the increased AOS content [21–23,31]. To verify the increased stability, we performed hot-water-vapor exposure tests, where the samples were placed 2 cm above 80°C hot water vapors for 1 min (hereafter referred to as hot-fogging tests). Pristine films (row 0, Figure 2) showed excellent transparency and resistance to hot-fogging tests. Additionally, increasing the AOS content within the film matrices improved their stability against water. As shown in Figure 2, the films with the highest AOS content of 5 $\alpha\%$ (hereafter referred to as PVP/NCP/AOS (5 $\alpha\%$) films) could maintain their robust antifogging properties, even after being submerged in water for more than 45 min. Therefore, the increased AOS content has improved the water stability of these hydrogel-based films through increased hydrogen bonding and electrostatic interactions [21–23].

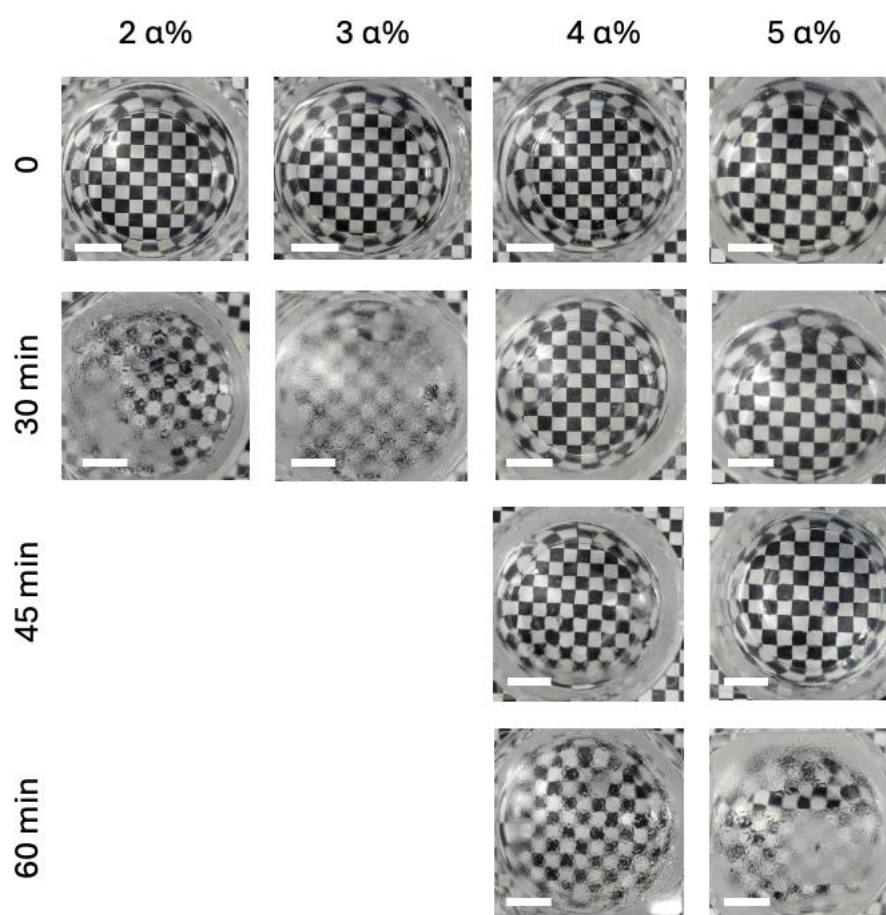


Figure 2. Optical micrographs of the PVP/NCP/AOS films prepared with different AOS content ($\alpha\%$) after being submerged in water for the specified amount of time and then demonstrated in hot-fogging tests. Scale bar is 1 cm.

When investigating hygroscopic properties, the films showed noticeable changes in mass when exposed to 80°C hot water vapors. PVP/NCP/AOS (5 $\alpha\%$) films could gain approximately 65% of their mass when pre-wetted for 10 min. However, even when left in high humidity environments ($>90\%$ relative humidity (R.H.)), there was no significant mass change, even after 24 h. Therefore, the hygroscopic nature of these films was affected by increasing the $\alpha\%$ content. We believe that because of the improved resistance to water, our films are less likely to absorb atmospheric water but otherwise can be swelled using hot water vapors. By increasing the cross-linking density, we also anticipated that the durability

of the antifogging properties would be improved. These PVP/NCP/AOS (5 $\alpha\%$) films maintained their robust antifogging for more than 3 months under laboratory conditions ($\sim 20^\circ\text{C}$ and 20–50% R.H.) or for 1 month under high humidity ($>90\%$ R.H.) conditions. No fogging was observed in simple breath tests. Therefore, the increased cross-linking density did improve the durability of the antifogging properties over our previously optimized films [23].

Because of the improved water stability, we expected that these PVP/NCP/AOS (5 $\alpha\%$) films (on glass slides), when submerged in water, would display stable underwater superoleophobicity in a manner similar to fish scales [27]. As expected, this film displayed underwater superoleophobicity, likely due to the formation of a stable thin layer of water on the surface [22,32] having an θ_S value of DIM was $\sim 164^\circ$ (Figure 3A) and a low CA hysteresis of less than 8° (θ_A/θ_R values of $\sim 171^\circ/\sim 163^\circ$).

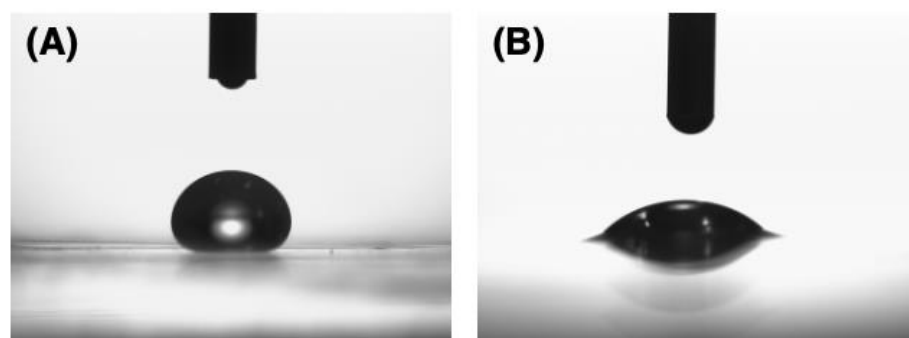


Figure 3. (A) A 3 μL droplet of DMC on the PVP/NCP/AOS (5 $\alpha\%$) film-coated glass slide submerged in DI water. Static CA was approximately 164° , showing underwater superoleophobicity. (B) Image of a 3 μL droplet of DIM when placed on a pre-wetted PVP/NCP/AOS (5 $\alpha\%$) film-coated PET sheet in air.

Judging from these excellent underwater oil-repellent properties, we expected that when these films were applied to PET sheets and bottles, they should also continue to exhibit such excellent oil-repellency once the film surface was sufficiently wetted with 80°C hot water vapors. However, PET has a T_g ranging from 65 to 80°C [33]; therefore, in order to prevent damaging the substrate, we reduced the drying temperature to 60°C to be sufficiently below the T_g and increased the drying time to compensate. The resulting average thickness using this adjusting drying method was 753.2 nm , which was within our average range for the substrates coated at 80°C and dried for 1 h. Therefore, we believed that these PVP/NCP/AOS (5 $\alpha\%$) film-coated PET substrates would be sufficient for anti-oil applications.

To verify that these PVP/NCP/AOS (5 $\alpha\%$) film-coated PET sheets were oil-repellent, we first measured the θ_S values of DIM on PET sheets with and without the films. The θ_S values of DIM were measured to be 40° and 26° for the coated and uncoated PET sheets, respectively, indicating statically oleophilic nature. As shown in Figure 3B, when attempting to measure the CAs in the presence of a thin layer of adsorbed water (pre-wetted by 80°C hot water vapors for 1 min), the θ_S and θ_A/θ_R values could not be measured precisely because of the formation of a wetting ridge [34]. However, a 3 μL droplet of DIM was observed moving at very low α value of $2\text{--}3^\circ$, indicating that the pre-wetted PVP/NCP/AOS (5 $\alpha\%$) film-coated PET sheet surfaces also showed excellent oil sliding properties in air.

In order to demonstrate the effectiveness of these pre-wetted PVP/NCP/AOS (5 $\alpha\%$) films, a simple study was performed where coated and uncoated PET sheets were partially immersed in a dyed canola oil bath. The PVP/NCP/AOS (5 $\alpha\%$) film-coated PET sheet surfaces demonstrated improved oil-repellency, as evidenced by the reduced amount of visible dye compared to uncoated PET sheets. This could be further improved by introducing a thin layer of adsorbed water to the topmost surface of the film. The PVP/NCP/AOS

(5 $\alpha\%$) film-coated PET sheets were exposed to 80 °C hot water vapors for 1 min, after which a condensed water layer was visibly observed. When these pre-wetted films were then submerged into the oil bath, very little oil stuck to the surface, and this oil could easily be removed through gravitational forces and light shaking (Figure 4). Therefore, we concluded that these films could support a sufficient water layer that enables oils to be easily removed, meaning that film surfaces showed excellent anti-oil adhesion properties.

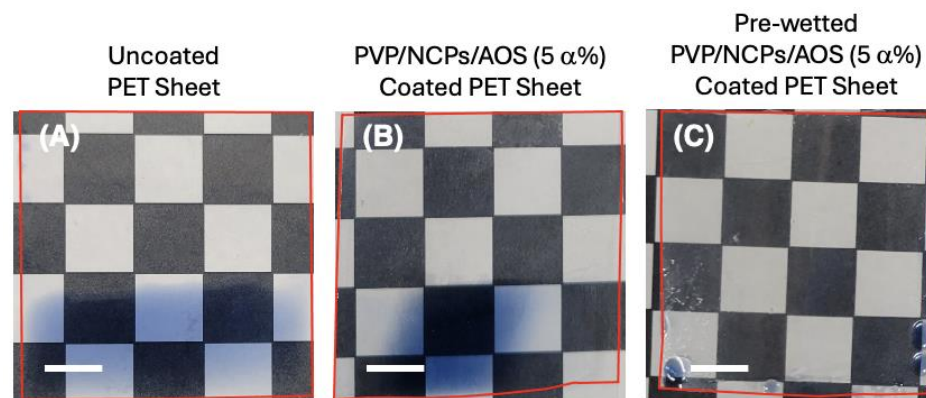


Figure 4. Optical images of PET sheets (B,C) with and (A) without coating of PVP/NCP/AOS (5 $\alpha\%$) films after being immersed in dyed canola oil bath. Red boxes outline the transparent PET sheets. Scale bar is 1 cm.

To further demonstrate the oil-repellency of these hydrogel-based films against other oils, some of the samples were immersed in octane and a silicone oil, as shown in Figure 5. When the pre-wetted PVP/NCP/AOS (5 $\alpha\%$) film-coated PET sheets were immersed in octane, they continued to display excellent oil-repellency, similar to canola oil. However, for the silicone oil, there was no significant difference in the amount of dyed oil remaining on the film surfaces. This may be attributed to PET being a material that is naturally resistant to silicone-based oils [33]; therefore, adding an oil-repelling layer does not show any visible improvement in the ability to repel silicone oils.

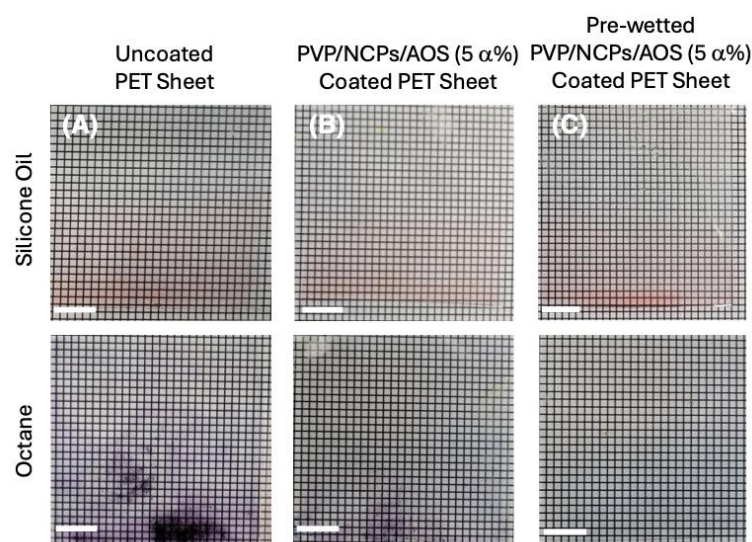


Figure 5. Optical images of PET sheets (B,C) with and (A) without coating of PVP/NCP/AOS (5 $\alpha\%$) films showing their ability to repel various oils from the surface. Scale bar is 1 cm. Checkered imaging used for contrast are 0.15 cm $\times$ 0.15 cm squares.

Furthermore, we investigated the durability of these water-driven oil-repellent properties at the oil/film interface. Since our films showed excellent water stability and hydrophilicity, we expected that these pre-wetted PVP/NCP/AOS (5 $\alpha\%$) film surfaces would

be able to repel oils for a long time, provided there was sufficient water to sustain the thin layer of water. To investigate this, we coated PET bottles with our PVP/NCP/AOS (5 $\alpha\%$) films and pre-wetted them with 80 °C hot water vapors for 10 and 20 min (Figure 6). When covered with oil, the pre-wetted film surfaces immediately began to show their excellent oil-repellency, as oil was quickly removed from the surface. In as little as 30 min, most of the oil was removed from the interior surfaces of the PET bottles for both samples, whereas the uncoated PET bottle still retained oil. Furthermore, these pre-wetted film surfaces exhibited excellent long-lasting oil-repellency for more than 5 weeks (ongoing). This clearly indicates that the water-thin layer on the topmost film surfaces was sufficiently stable at the oil/film interface, even with only 10 min of pre-treatment. The increased hydrogen bonding due to the increased AOS content may not only have resulted in the increased stability against bulk water and high relative humidity conditions but also formed strong interactions with the water at the surface, resulting in a stable thin layer of water on the surface. With the increasing post-treatment time, the initial oil-repellency was improved, but the durability slightly decreased. Since canola oil is used as an emulsifier in other oil/water applications [35], we thus believe that it may have extracted the excess water formed from the increased post-treatment time and removed some of the absorbed water along with it, reducing the overall effectiveness of the oil-repellent properties. This is supported by the fact that for coated PET bottles, after being pre-wetted for 20 min, their films initially supported a 133% increase in mass (as opposed to 65% for 10 min of pre-wetting), yet after approximately 24 h, excess water was visible within the sealed container that had 20 min of pre-wetting, indicating that excess water was slowly being expelled from the hydrogel-based films. However, PVP/NCP/AOS (5 $\alpha\%$) film-coated PET bottles that were pre-wetted for 10 min had no excess water visible.

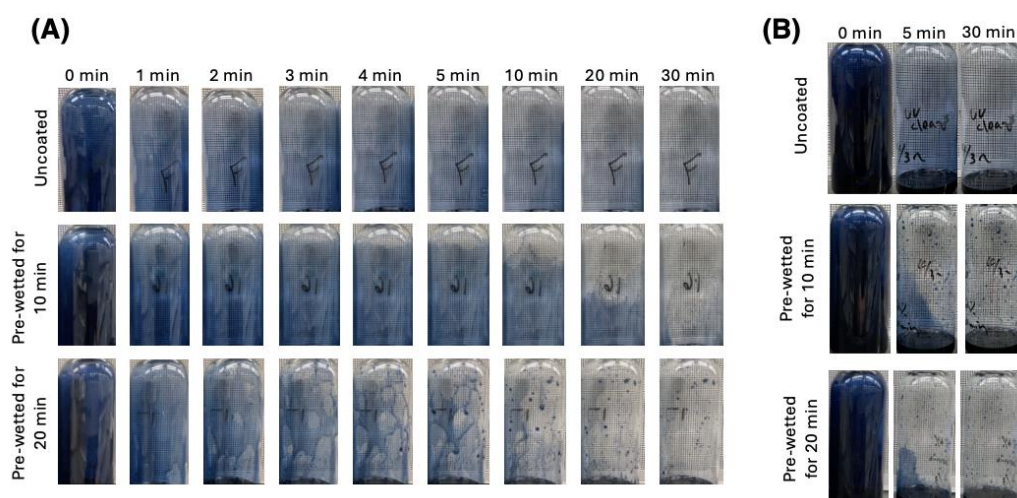


Figure 6. Optical images of PET bottles with and without coating of pre-wetted PVP/NCP/AOS (5 $\alpha\%$) films showing their ability to repel dyed canola oil after (A) 0 and (B) 5 weeks.

We thus concluded that improving the water stability of our hydrogel-based films by increasing AOS content would allow the formation of a stable water-thin layer at the topmost region of the films, as well as a significantly extended lifetime for those films. This would greatly help to repel organic oils from PET substrates, providing an environmentally friendly path for creating transitory anti-oil adhesion coatings to improve PET bottles recycling as well as developing other sustainable methods to create durable yet temporarily cross-linked coatings for oil repelling applications.

4. Conclusions

We have successfully improved the water stability of our PVP/NCP/AOS hydrogel-based films by increasing their cross-linking density through increasing the AOS content. Thanks to this effect, a stable water-thin layer was found to be successfully formed on the

topmost film surfaces. When our water-stable hydrogel-based film was coated onto the inside of PET substrates and pre-wetted using 80 °C hot water vapors, they could effectively repel various oils and were able to maintain their excellent anti-oil adhesion properties for more than 5 weeks (ongoing). By using a more powerful mixing method, we were able to incorporate more AOS into our precursor solutions. This successfully increased the water stability through the formation of a stable network in our transparent hydrogel-based films, leading to stable, long-lasting, and durable anti-oil adhesion properties. In our case, the use of any harmful long-chain perfluorinated compounds, which have been widely used to achieve oil repellency, is not necessary. This may help to develop other sustainable coatings and improve the recyclability of PET bottles in both a human and environmentally friendly manner without relying on conventional surface perfluorination.

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Conflicts of Interest: The authors declare no conflicts of interest.

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