
Polydimethylsiloxane-coated textiles with minimized microplastic pollution

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Supplementary Text 1. The detailed analysis of the ATR FTIR peak positions

Supplementary Fig. 2a shows the ATR FTIR spectra of neat MPTMS and the H₂O₂-modified MPTMS. The neat MPTMS has two characteristic peaks at 1090 cm⁻¹ and 2550 cm⁻¹ (see curve b1), attributed to the stretching vibrations of Si–O–C and S–H groups, respectively.^{1,2} After oxidation by hydrogen peroxide, two new peaks of S=O appeared at 1030 cm⁻¹ and 1415 cm⁻¹, indicating that the mercapto groups (S–H) of MPTMS had been oxidized to sulphonic acid groups (see curve b2). The absorption peak at 1108 cm⁻¹ corresponds to the stretching vibration of Si–O–Si groups,^{3–5} implying that some hydrolyzed-MPTMS monomers had polycondensed and oligomerized. However, the strong absorption peak at 1636 cm⁻¹ confirms the presence of silanol groups (Si–OH),⁶ necessary for grafting the PDMS brushes on the surface of the nylon fabrics and indicates that most of the hydrolyzed methoxy groups remained as silanols and not oligomeric reaction products. The modified MPTMS did not show any S–H absorption peaks after oxidation (see curve b2), highlighting the successful formation of the primer as intended.

To validate the primer deposition and grafting of PDMS brushes on the surface of the nylon-6,6 fabric, ATR FTIR was also employed. Supplementary Fig. 2b shows the ATR FTIR spectra of untreated and primer-PDMS brush treated nylon-6,6 fabrics. First, it is evident that there are two characteristic absorption peaks positioned at 1628 cm⁻¹ and 1533 cm⁻¹ for both the fabrics, corresponding to the stretching and in-plane bending vibrations of nylon's C=O (amide I) and N–H (amide II) groups, respectively (see curve c1 and c2).⁷ After treating the fabric with the primer and PDMS brushes, a new peak at 1053 cm⁻¹ was observed (see curve c2), corresponding to the stretching of the S=O group derived from the ionic bonding between the nylon fabric and the primer.⁸ In addition, the primer-PDMS treated fabric showed additional absorption peaks of Si–O and Si–O–Si at 804.7 cm⁻¹ and 1108 cm⁻¹, respectively (see curve c2).^{5,9} These peaks arise from the grafting of both the primer layer and PDMS brushes on the surface of the fabrics.

Supplementary Text 2. Physical and comfort properties of fabrics

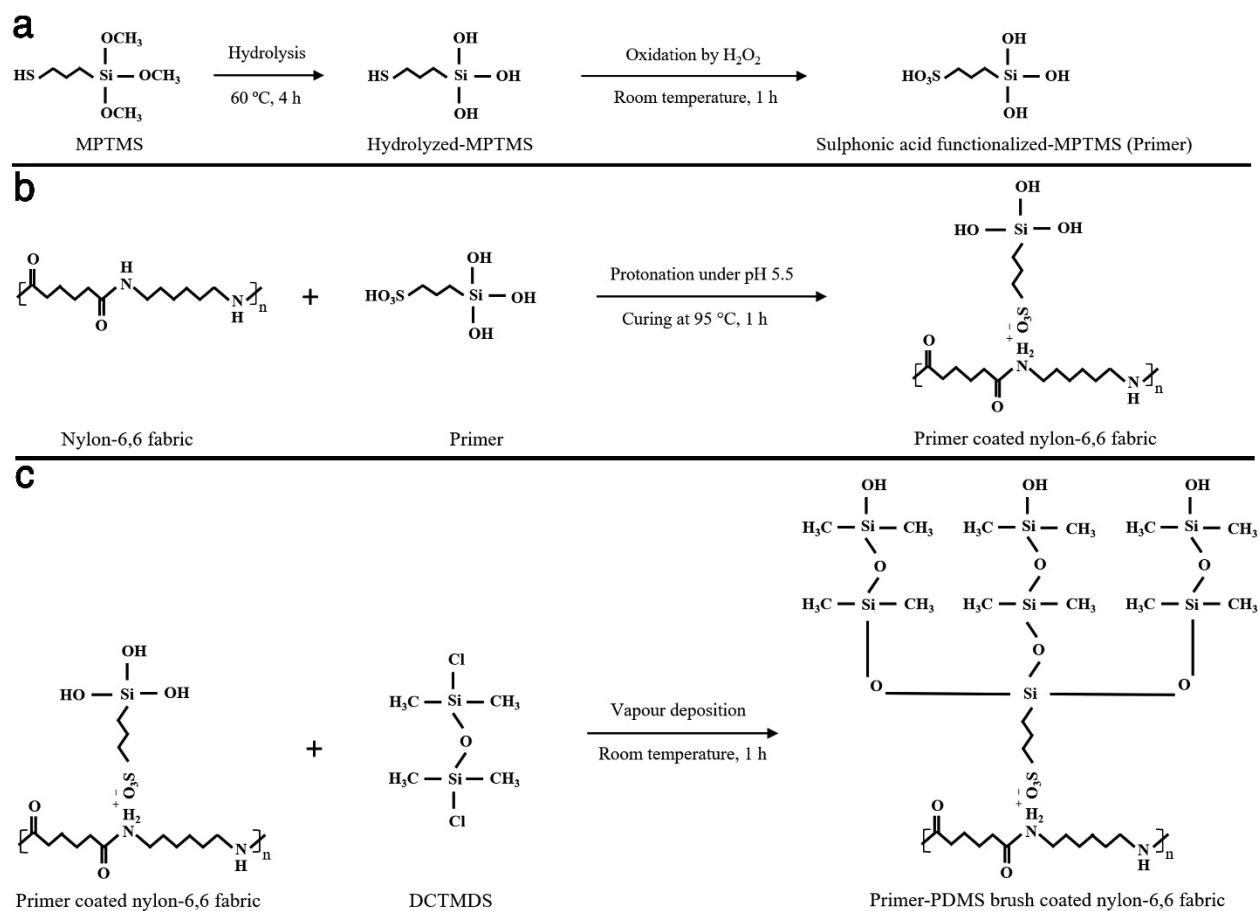
While our study indicated that the primer-PDMS brush coating was successful, the coating would only find real-world usage if other fabric properties were not degraded. Fabric softness is a fundamental fabric

characteristic in the textile industry and is assessed via a fabric's bending rigidity (mg.cm), for example using the BS 3356-1990 standard.¹⁰ A schematic of the bending test used in this study is presented in Supplementary Fig. 3a. The bending rigidity of the untreated and treated nylon fabrics is shown in Supplementary Fig. 3b. The bending rigidity of the primer-PDMS brush treated nylon fabric was statistically equivalent to that of the untreated fabric (p-value: 0.0628), indicating that the coating did not alter the mass of the fibers and maintained good softness of the treated fabrics. The handle of the fabric, in particular the shear rigidity and hysteresis of shear rigidity of the fabric, was determined following a Kawabata Evaluation method developed for fabrics.¹¹ The shear values and curves of the untreated, softener treated, and primer-PDMS brush treated nylon fabrics are shown in Supplementary Table 1 and Supplementary Fig. 4, respectively. The shear behavior of softener treated fabrics slightly changed compared to untreated fabrics, with an average reduction of ~7 % in shear rigidity, G (see Supplementary Table 1). The primer-PDMS brush finishing resulted in an average reduction of ~31 % in shear rigidity. Similar results were observed for the shear hysteresis 2HG at 0.5 degree and 2HG5 at 5 degrees. The greater than 73% reduction in shear hysteresis 2HG and 63 % in 2HG5 further indicates that the finishing treatment significantly lowers inter-fiber and inter-yarn friction. This corroborates our ball-on-disc tribology measurements.

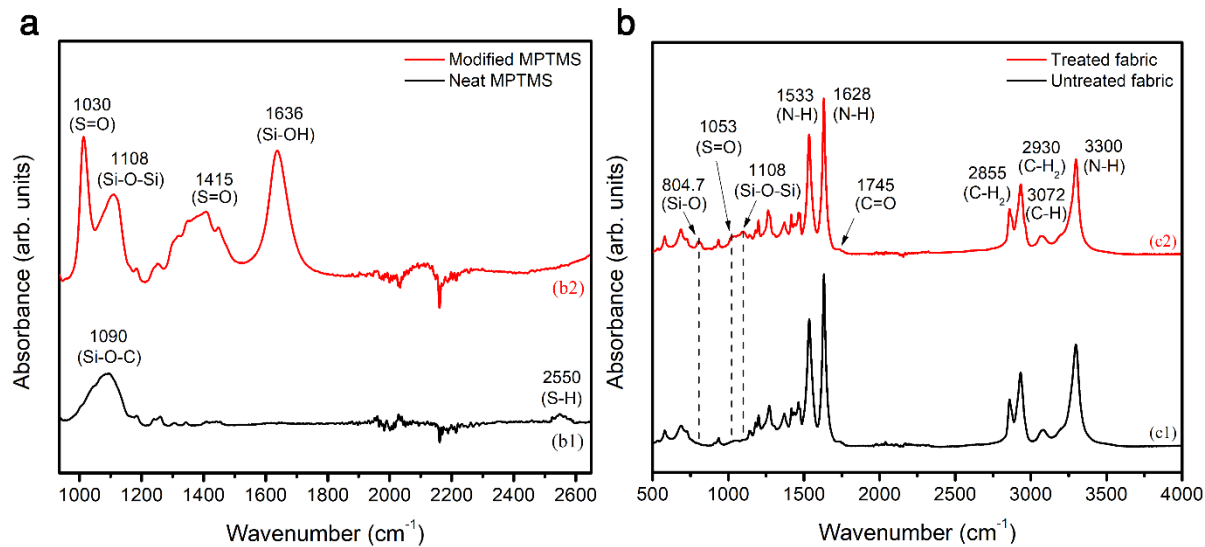
Air permeability is another fundamental textile property and an important factor in the comfort of a fabric.^{12,13} The air permeability of the untreated and treated fabrics are shown in Supplementary Fig. 5. The air permeability of the fabric was statistically unchanged before and after the primer-PDMS coating deposition (p-value: 0.5108). This was expected, as the air permeability of fabrics mainly arises from the open voids between yarns, and the SEM images of the primer-PDMS brush treated fabrics showed that the finishing treatment did not block the fiber spacing of the fabrics (see Fig. 1d(iv-vi)). Together with the hand feel results, these characterizations indicated the low-friction fabric finish developed in this work would not decrease the comfort of nylon garments incorporating the coating.

Supplementary Table 1: Shear rigidity (G) and shear hysteresis (2HG and 2HG5) of the untreated, softener treated, and primer-PDMS brush treated nylon-6,6 fabrics.

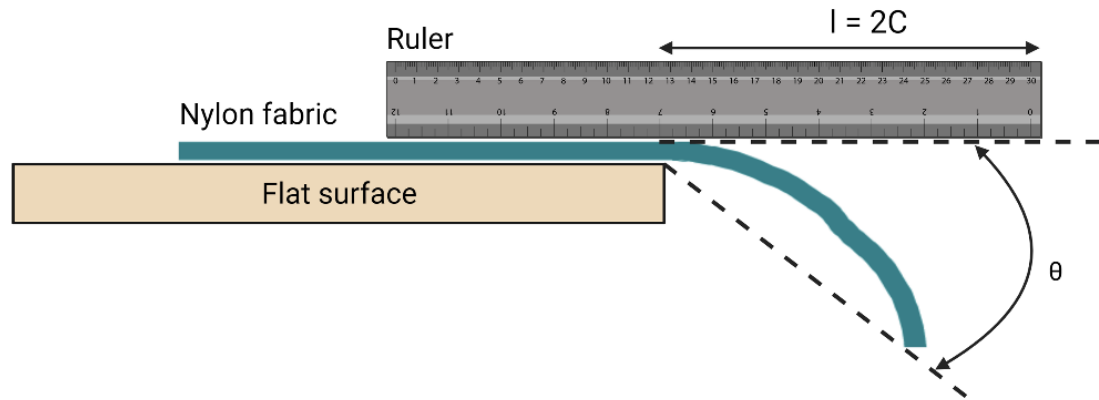
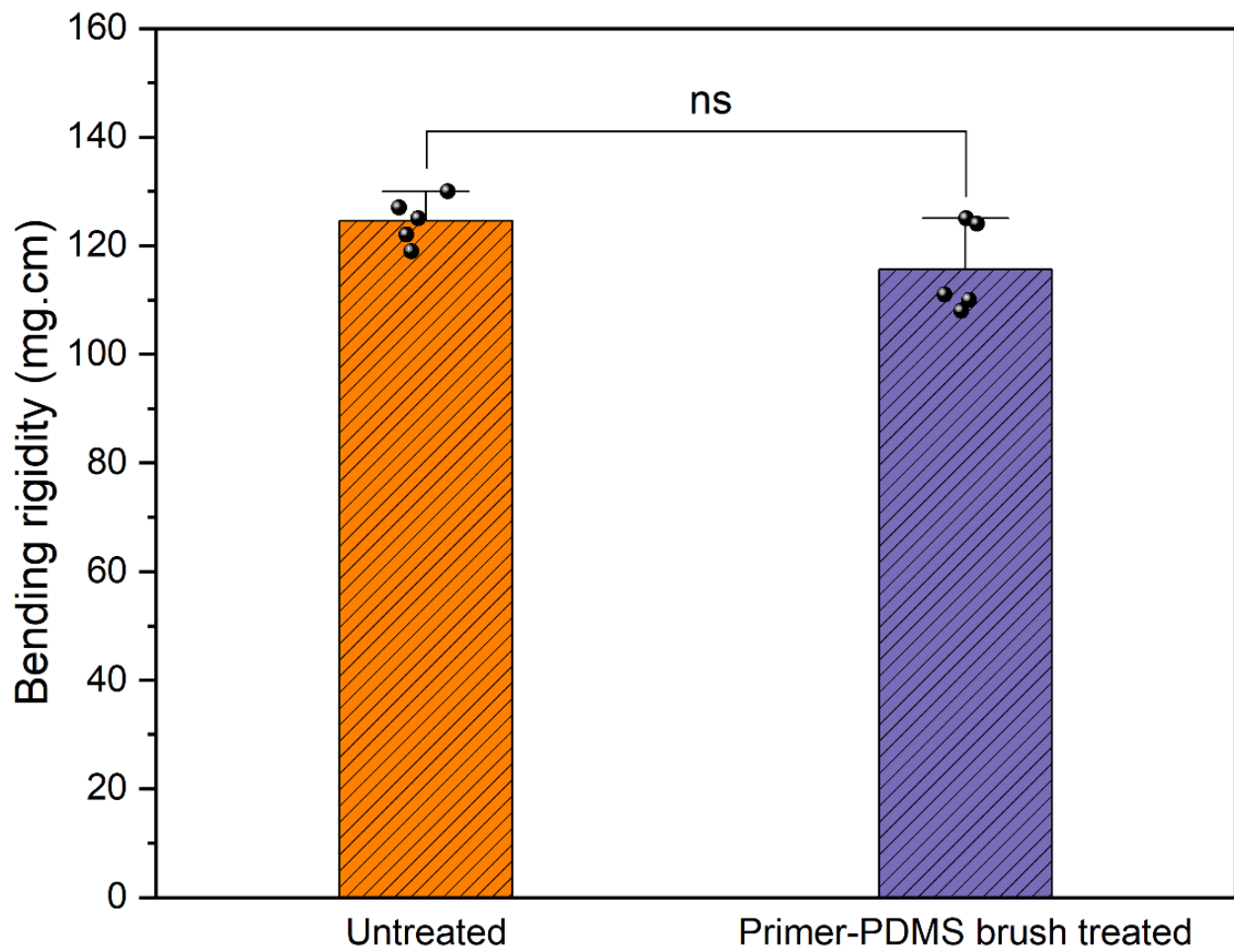
Samples	$G, \text{gf cm}^{-1}, \times 10^{-1}$	2HG at 0.5 degree, $\times 10^{-1}$	2HG5 at 5 degrees, $\times 10^{-1}$
Untreated fabric	9.5	9.4	30
Softener treated fabric	8.8	4.3	23
Primer-PDMS brush treated fabric	6.6	2.5	11



Supplementary Figure 1. Reaction schemes of the primer-PDMS brush coating. (a) Synthesis of sulphonic acid functionalized MPTMS (primer). (b) Primer reaction to nylon-6,6. (c) Grafting of PDMS brushes to the primer-coated nylon-6,6 fabric. Note that a single molecule of DCTMDS molecule is shown bonded to the fabric surface in c, whereas in reality the DCTMDS polymerizes to the PDMS brush structure.

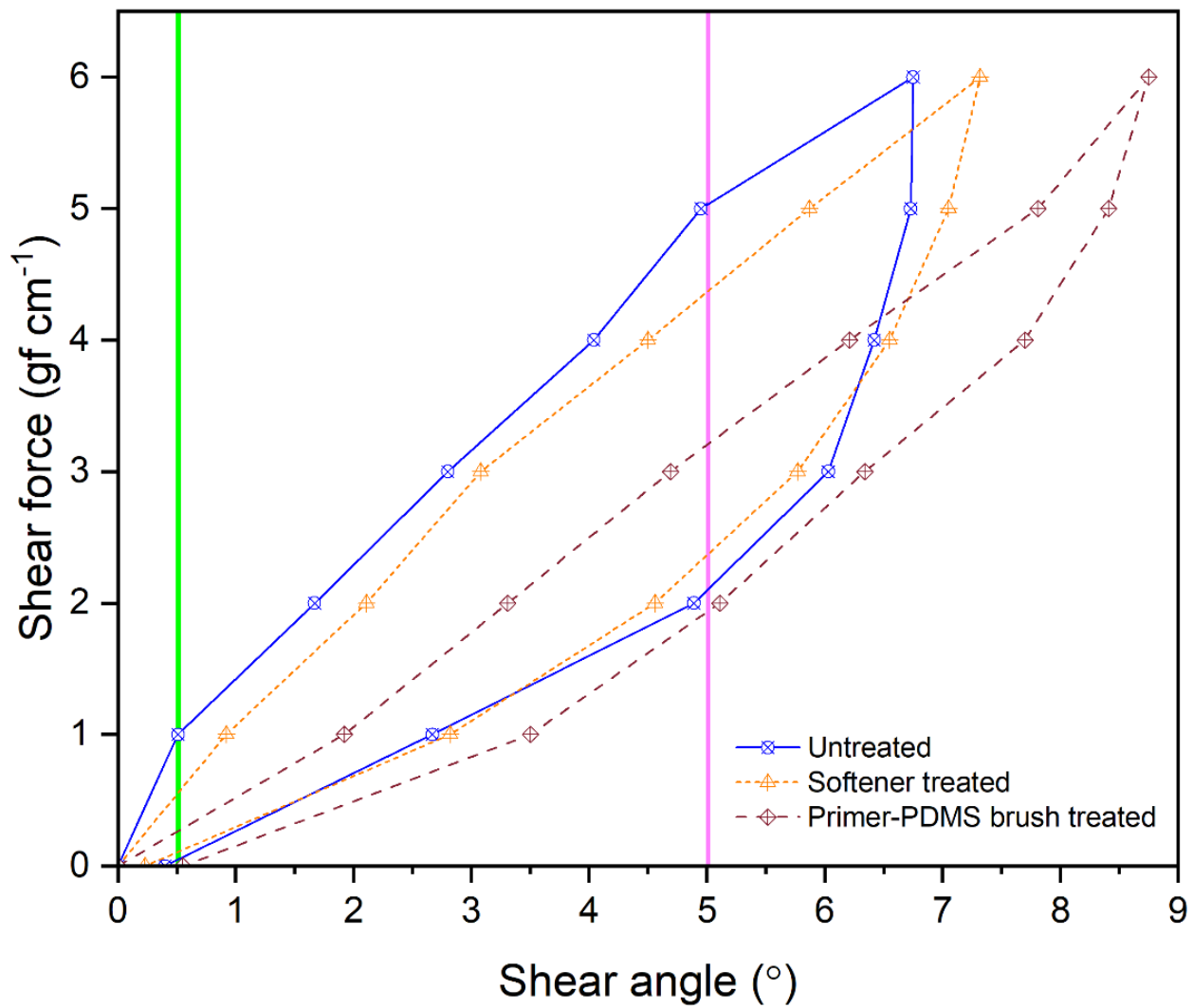


Supplementary Figure 2. (a) ATR FTIR spectra of the primer, showing the conversion from neat MPTMS to sulphonic acid functionalized MPTMS. (b) ATR FTIR spectra of untreated and primer-PDMS brush treated nylon-6,6 fabric.

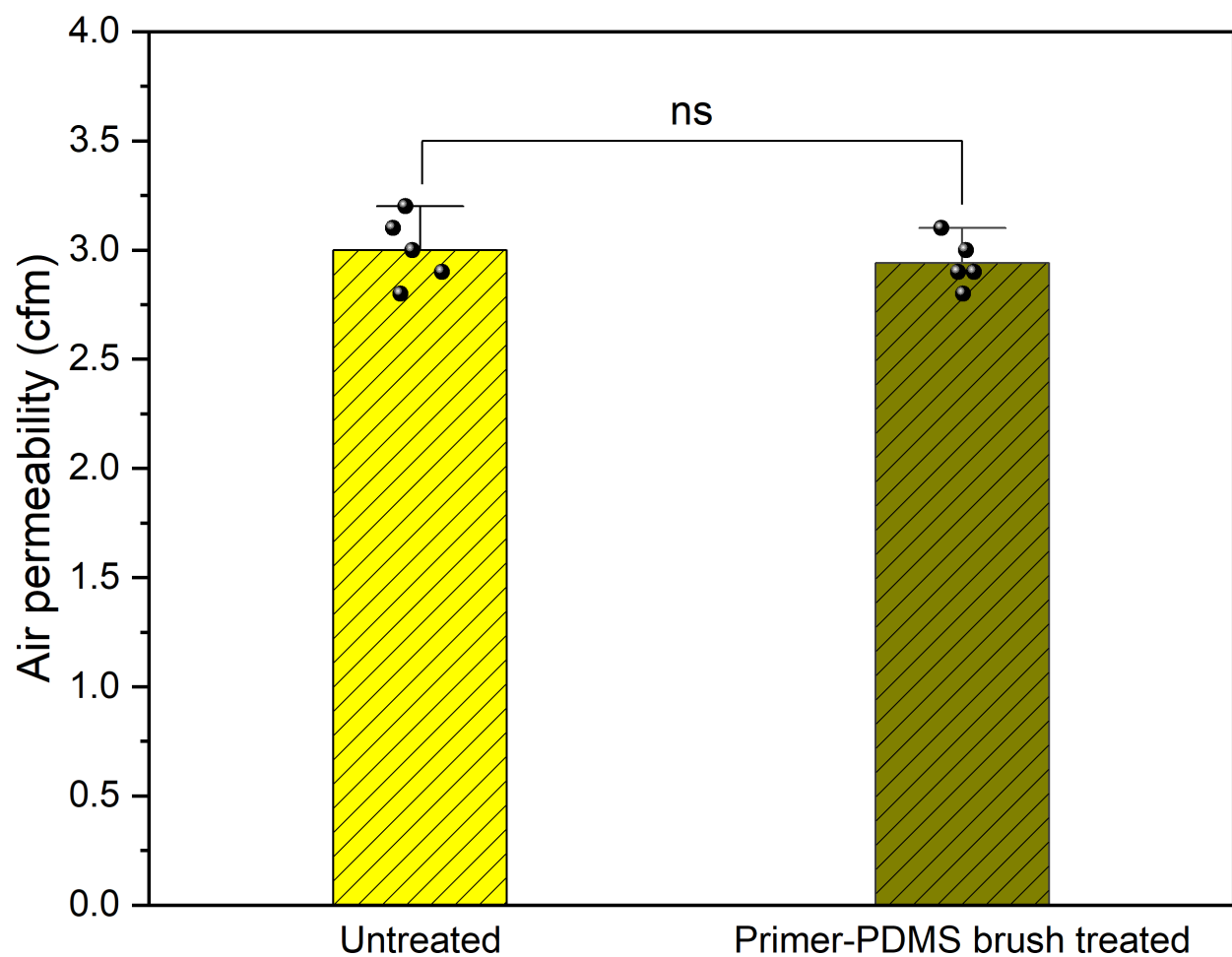
a**b**

Supplementary Figure 3. (a) Schematic diagram of bending test according to the BS 3356-1990 standard.

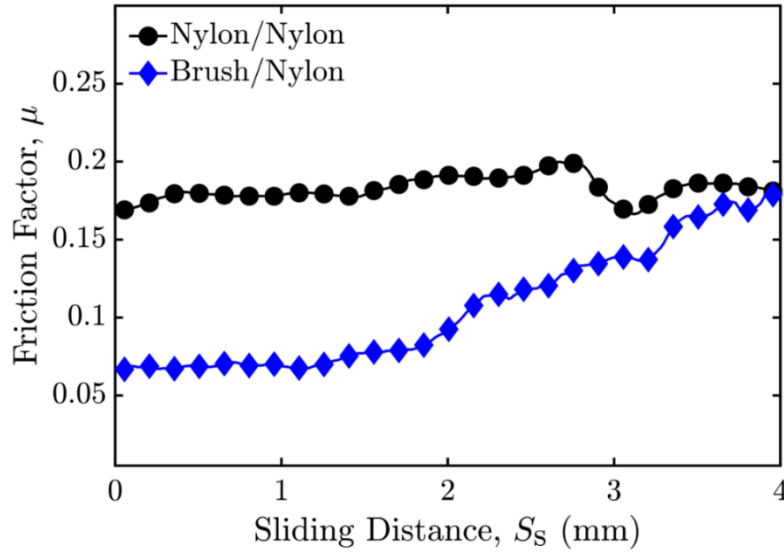
(b) Bending rigidity of untreated and primer-PDMS brush treated nylon-6,6 fabrics. ns = no significance (p -value > 0.05). Error bars are the mean $\pm$ 1 SD and here $N = 5$.



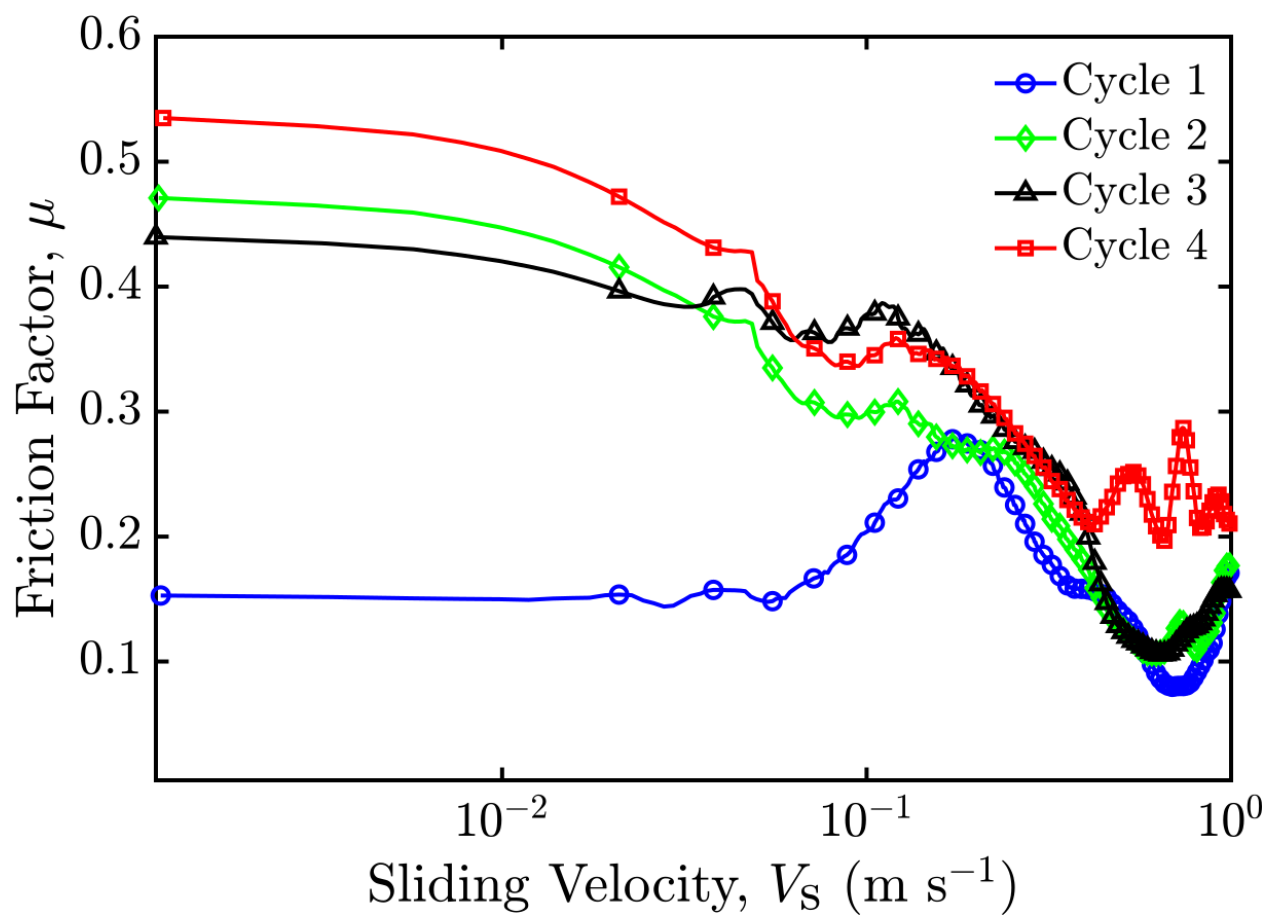
Supplementary Figure 4. Shear curves of the untreated, softener treated, and primer-PDMS brush treated nylon-6,6 fabrics according to a Kawabata analysis.



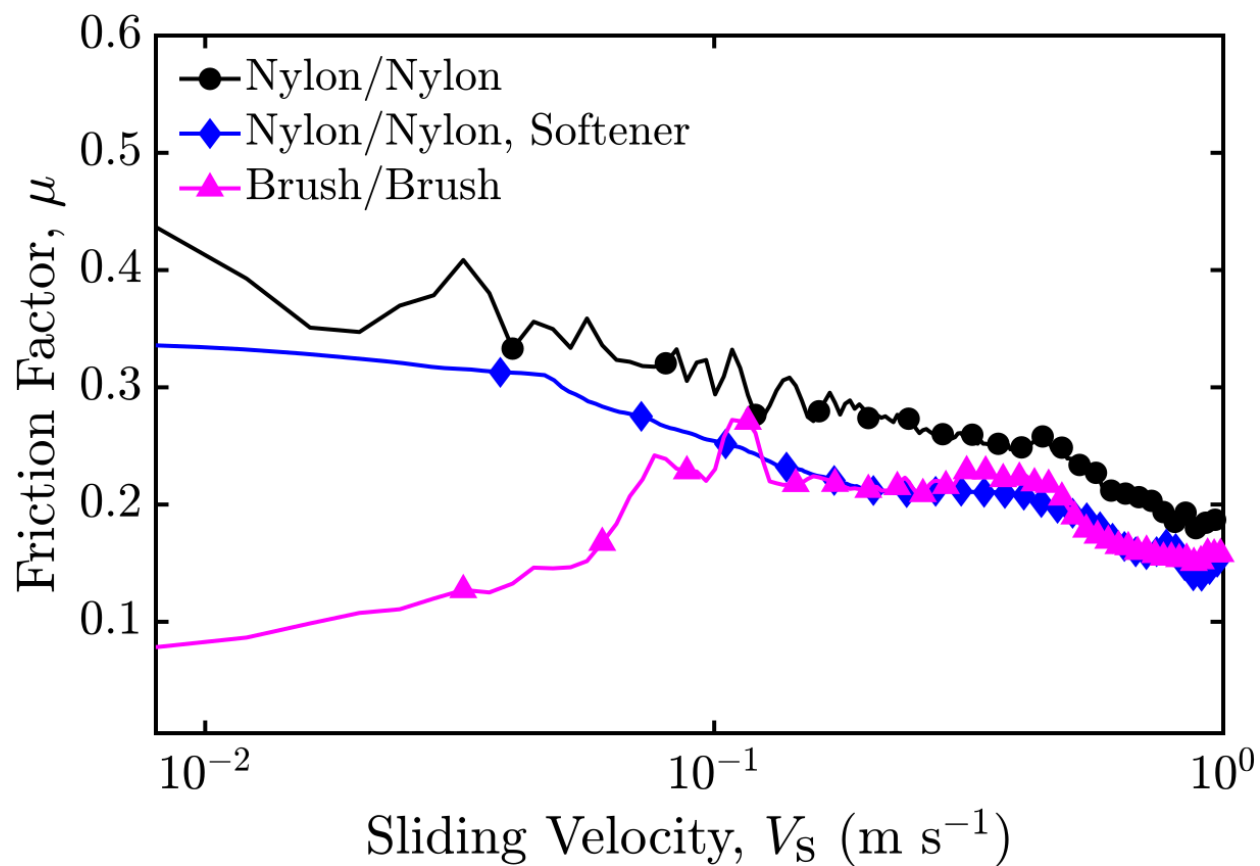
Supplementary Figure 5. Air permeability of the untreated and primer-PDMS brush treated nylon-6,6 fabrics, according to ASTM D737-96 standard. ns = no significance ($p\text{-value} > 0.05$). Error bars are the mean $\pm$ 1 SD and here $N = 5$.



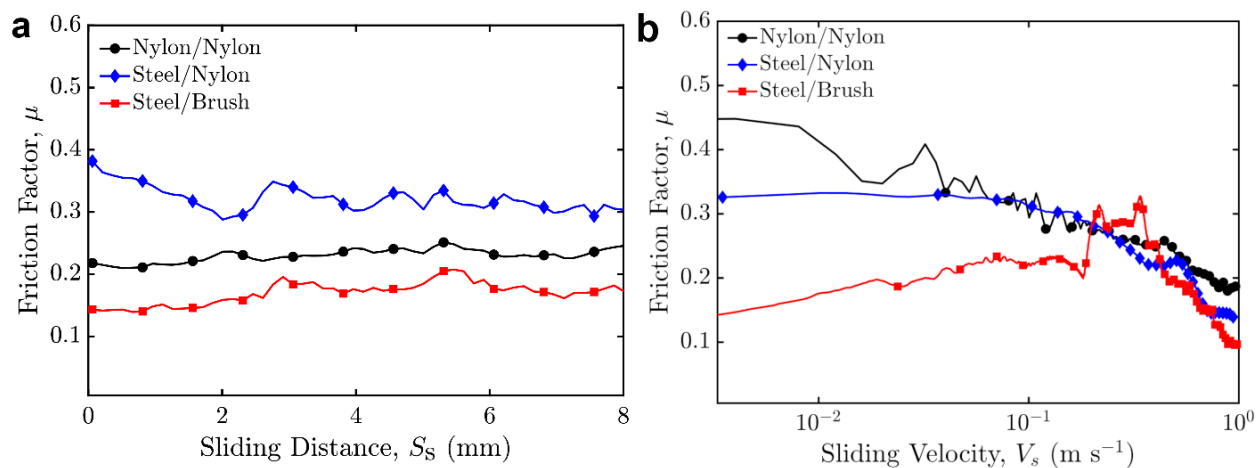
Supplementary Figure 6. Dry friction measurements of nylon/nylon and brush/nylon samples. For the mixed interface (brush/nylon) the friction was still reduced $\sim 29\%$ (p-value: 0.01262), and this was independent of whether the ball or disc was coated (p-value: 0.09967, ‘ns’ = no significance in Fig. 4b). However, in the case of the PDMS brush-coated ball sliding on the bare nylon disc (brush/nylon arrangement), the friction factor began to increase for longer sliding distances, and eventually approached the friction factor of the bare nylon/nylon interface. Given that nylon is itself abrasive, as evidenced by the microfiber shedding experiments, this result suggests that the PDMS brushes were being removed from the nylon ball during the tribological analysis. While at first glance this would indicate a durability issue for the coating, in reality this tribological interface is far from practical. Assuming Hertzian contact between the ball and disc, the diameter of the circular area of contact during the tribology experiments was $\approx 200 \mu\text{m}$, or just 5% of the total sliding distance. This would be comparable to a fabric with 95% bare nylon fibers—far from representative of a coated textile. In contrast, the nylon/brush configuration, where no increase in friction was observed, would represent a fabric with 50% coated fibers and 50% bare fibers (as any abraded coating is replaced by fresh coating during sliding). While still demonstrative of a poorly finished fabric, these results instead indicate that the coating remains effective at reducing friction even when roughly half abraded away and would thus continue to lessen microfiber shedding throughout the lifetime of the garment.



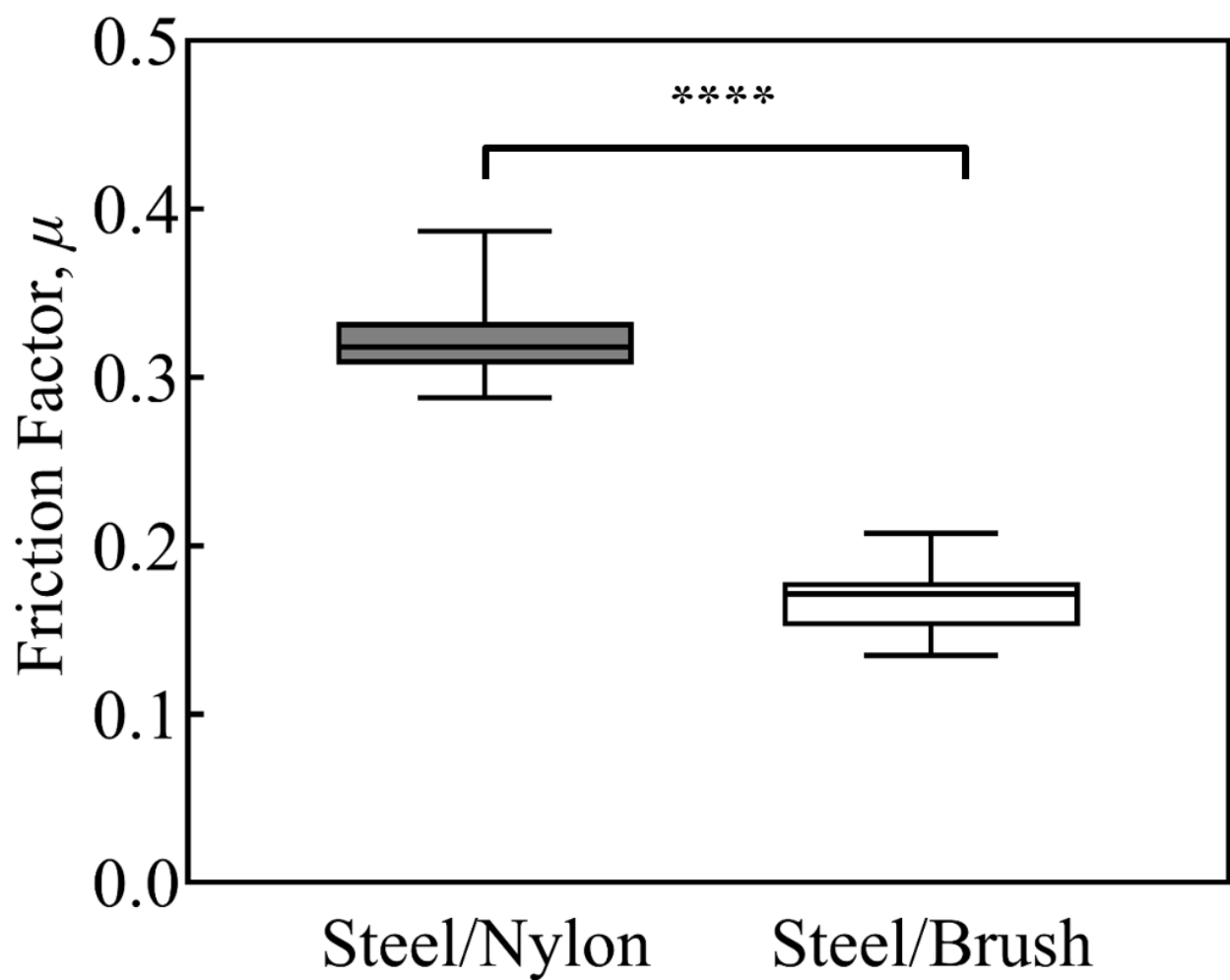
Supplementary Figure 7. Stribeck curves for sliding bare nylon ball on primer-PDMS brush coated nylon discs. The wet friction measurements were repeated four consecutive times, indicating wear of the coating with repeated tribology testing.



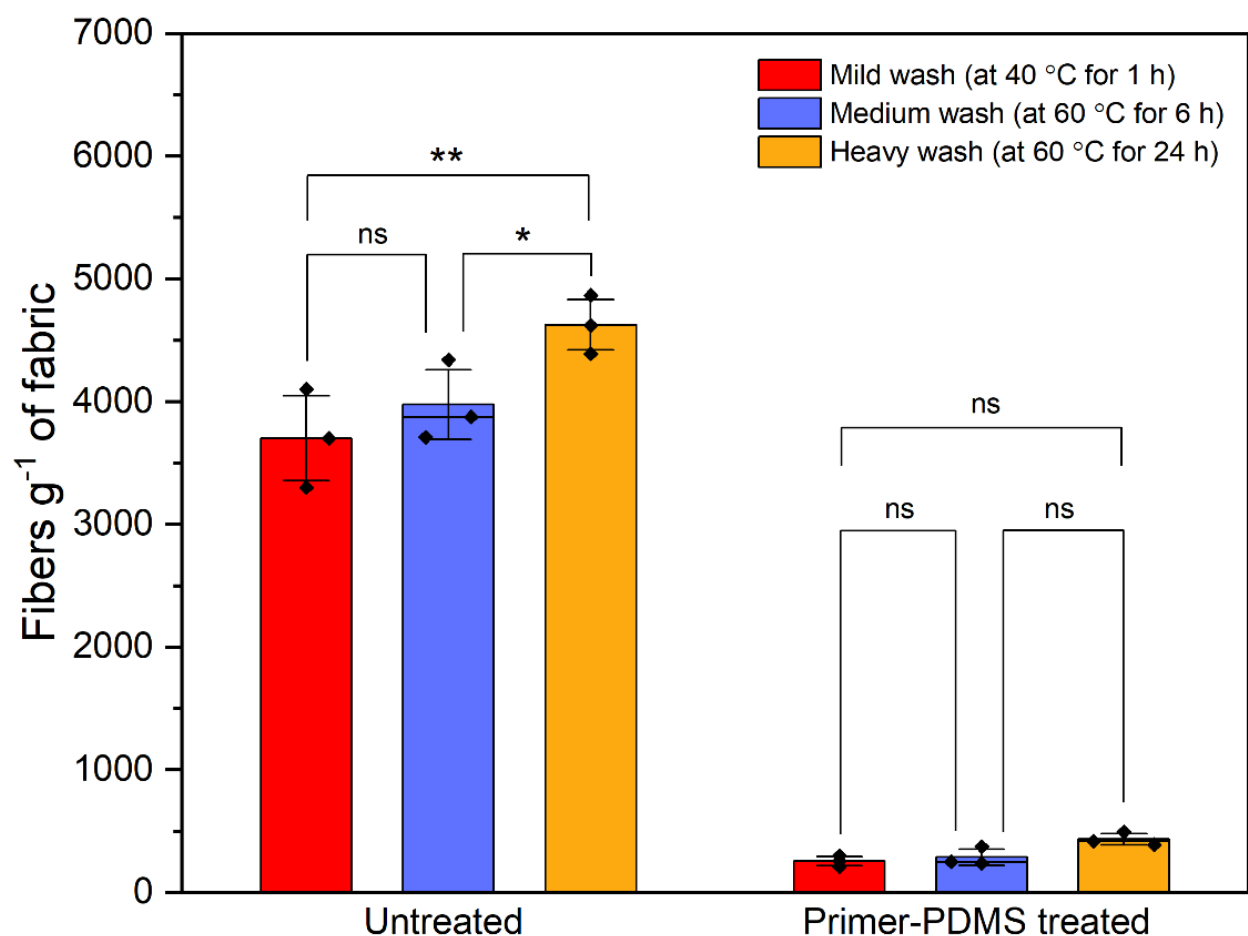
Supplementary Figure 8. The effect of commercial fabric softener on the friction of nylon. The untreated and primer-PDMS brush treated nylon's wet friction are shown for comparison. All tests were repeated at least four times.



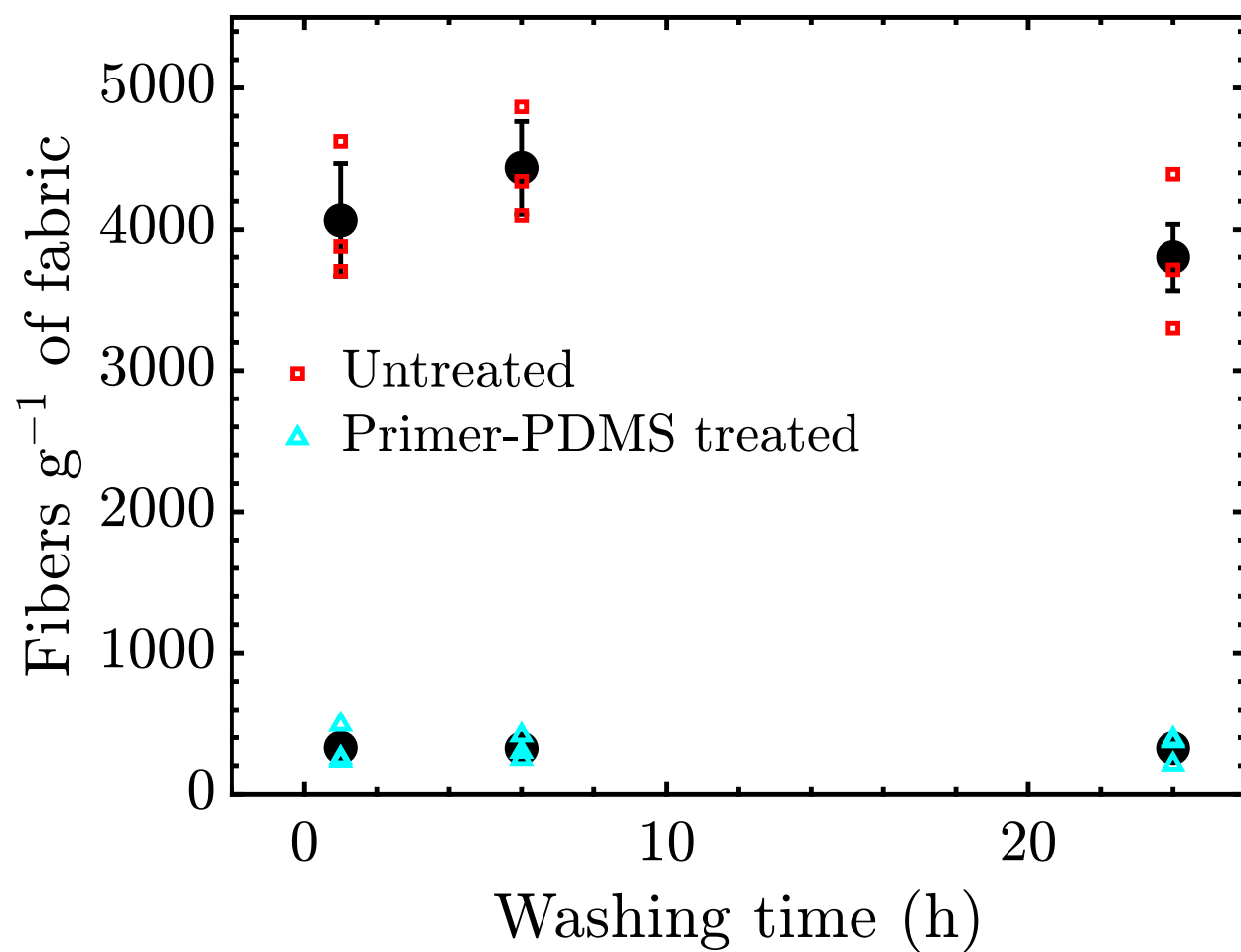
Supplementary Figure 9. To better simulate the walls of a washing machine, tribological measurements were also taken between steel balls and nylon discs, either uncoated or treated with the primer-PDMS brush finish. (a) Dry friction factor results of the two different sample arrangements over an 8 mm sliding distance. (b) The Stribeck curves (wet friction) results for bare and primer-PDMS brush coated nylon surfaces, again using a steel ball.



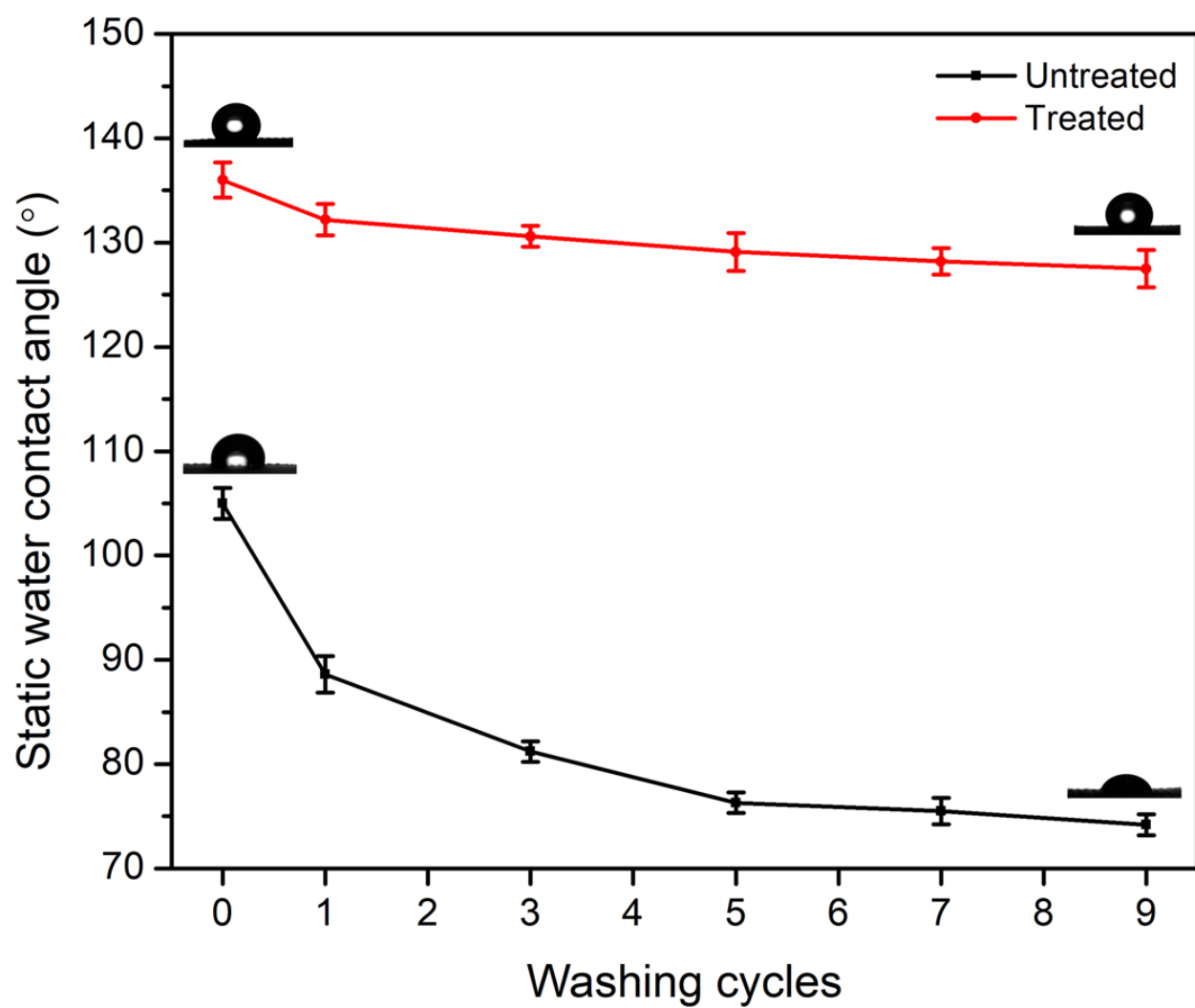
Supplementary Figure 10. Dry friction factor between steel and nylon, either treated or untreated. The friction factors were measured over an 8 mm sliding distance. **** indicates a Student's t-test p-value < 0.001. The box presents the first quartile, mean, and the third quartile from lower to higher amounts. The minimum and maximum are shown as lowest and highest whiskers, respectively.



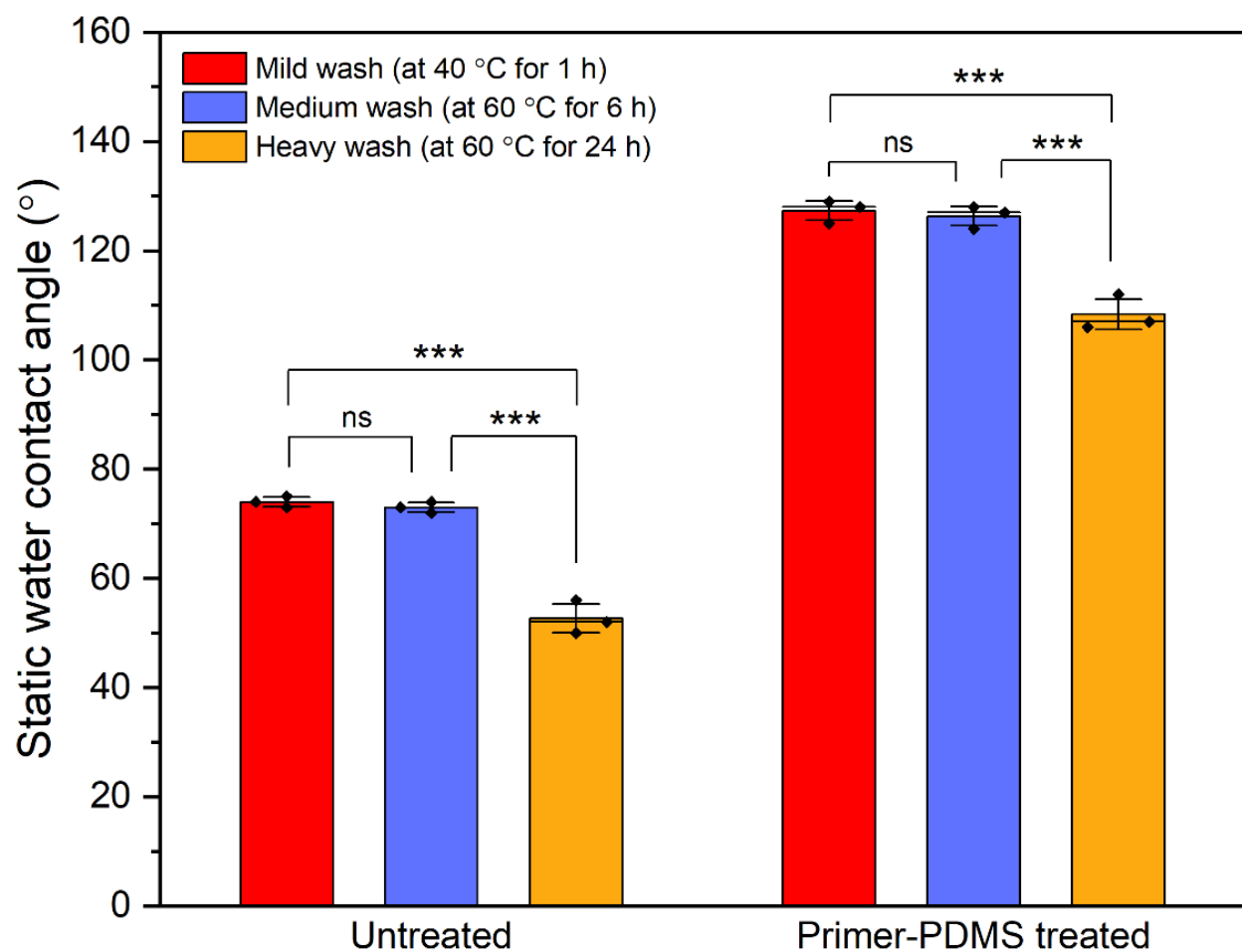
Supplementary Figure 11. The mean number of microplastic fibers (MPFs) per gram of fabric released from untreated and primer-PDMS-brush-treated fabrics as a function of washing conditions. Error bars are the mean $\pm$ 1 SD and here N = 3. * indicates a Student's t-test p-value < 0.05, ** indicates a Student's t-test p-value < 0.01, and ns = no significance (p-value > 0.05). For the untreated fabric the mild wash (at 40 °C for 1 h) produced statistically less microfibers than the heavy wash (at 60 °C for 24 h), and the medium wash (at 60 °C for 6 h) produced statistically less MPFs than the heavy wash. For the primer-PDMS brush treated fabric, all three wash cycles produced a statistically similar number of MPFs.



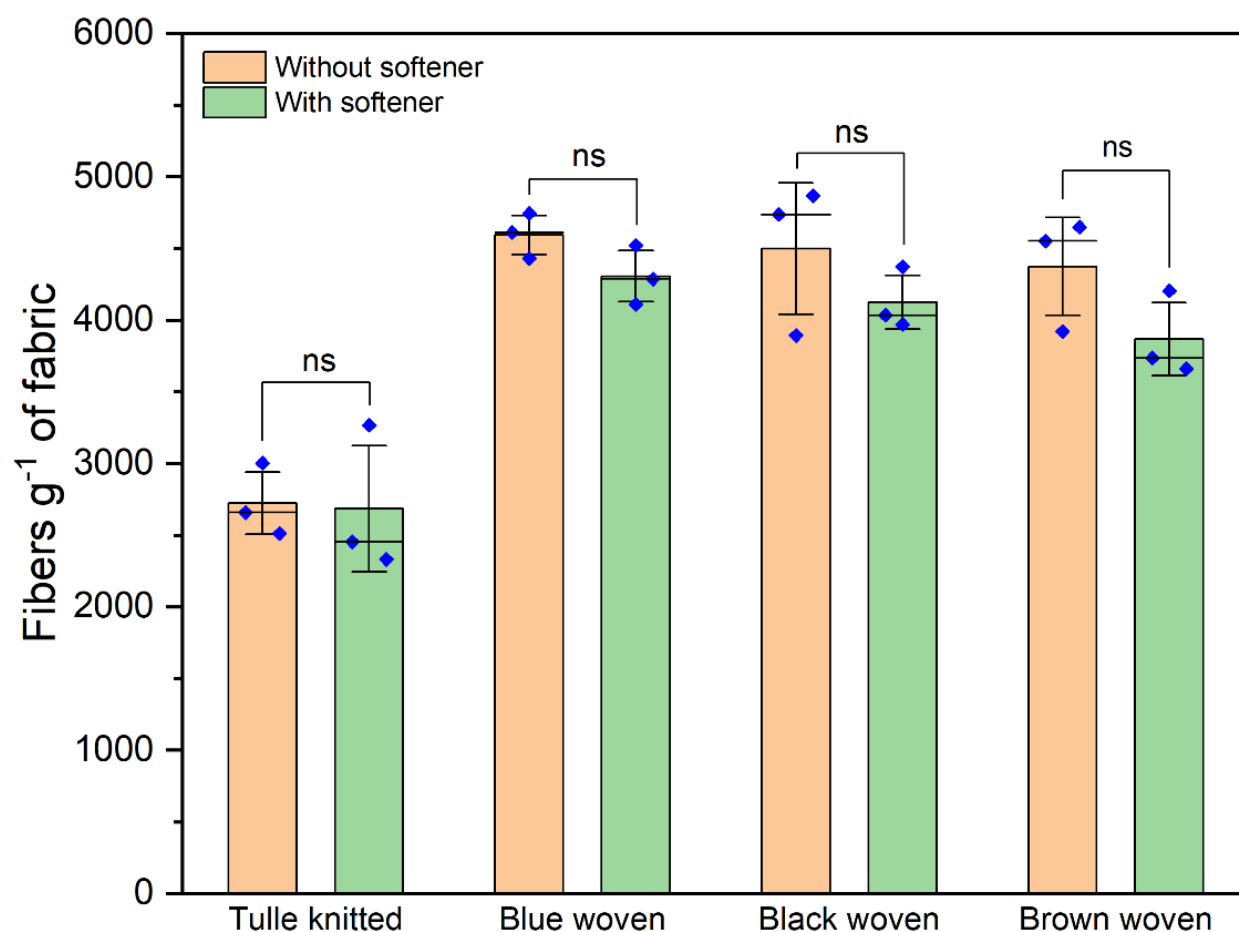
Supplementary Figure 12. The mean number of microplastic fibers per gram of fabric released from untreated and primer-PDMS-brush-treated fabrics, plotted against different washing times. Note that the 1 h wash was conducted at 40 °C whereas the 6 h and 24 h washes were done at 60 °C. Error bars are the mean $\pm$ 1 SD and here N = 3.



Supplementary Figure 13. Static water contact angles of the untreated and primer-PDMS brush treated nylon-6,6 fabrics as a function of the number of washing cycles. The inserts in image show deposited water droplets before and after washing the fabric. Error bars are the mean $\pm$ 1 SD and here N = 3.



Supplementary Figure 14. Static water contact angles of the untreated and primer-PDMS treated nylon fabrics as a function of washing conditions. Error bars are the mean $\pm$ 1 SD and here N = 3. *** indicates a Student's t-test p-value < 0.001 and ns = no significance (p-value > 0.05). For both the untreated and treated fabrics, only the heavy wash (at 60 °C for 24 h) altered the wettability of the fabric statistically significantly.



Supplementary Figure 15. The mean number of microplastic fibers (MPFs) per gram of fabric released from different commercially available nylon fabrics treated with softener and without softener. Error bars are the mean $\pm$ 1 SD and here N = 3. The addition of a fabric softener did not reduce the shedding of MPFs statistically significantly, as compared to the untreated fabrics. ns = no significance (p-value > 0.05).

References

1. Schramm, C. High temperature ATR-FTIR characterization of the interaction of polycarboxylic acids and organotrialkoxysilanes with cellulosic material. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **243**, 118815 (2020).
2. Krishnakumar, V. & John Xavier, R. FT Raman and FT-IR spectral studies of 3-mercapto-1,2,4-triazole. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **60**, 709–714 (2004).
3. Lahiri, S. K., Zhang, C., Sillanpää, M. & Liu, L. Nanoporous NiO@SiO₂ photo-catalyst prepared by ion-exchange method for fast elimination of reactive dyes from wastewater. *Mater. Today Chem.* **23**, 100677 (2022).
4. Jannatun, N., Taraqqi-A-Kamal, A., Rehman, R., Kuker, J. & Lahiri, S. K. A facile cross-linking approach to fabricate durable and self-healing superhydrophobic coatings of SiO₂-PVA@PDMS on cotton textile. *Eur. Polym. J.* **134**, 109836 (2020).
5. Kumar Lahiri, S. & Liu, L. Fabrication of a Nanoporous Silica Hydrogel by Cross-Linking of SiO₂–H₃BO₃–Hexadecyltrimethoxysilane for Excellent Adsorption of Azo Dyes from Wastewater. *Langmuir* **37**, 8753–8764 (2021).
6. Mir, N., Jalilian, S., Karimi, P., Nejati-Yazdinejad, M. & Khammarnia, S. 1,3,4-Thiadiazol derivative functionalized-Fe₃O₄@SiO₂ nanocomposites as a fluorescent probe for detection of Hg²⁺ in water samples. *RSC Adv.* **8**, 21745 (2018).
7. Yan, W. *et al.* Surface modification of reverse osmosis membrane with tannic acid for improving chlorine resistance. *Desalination* **498**, 119919 (2021).
8. Douthwaite, F. J. & Lewis, D. M. The formation of cysteine-S-sulphonate groups in wool and the effect on shrink-resistance. *J. Soc. Dye. Colour.* **110**, 304–307 (1994).
9. Withnall, R. & Andrews, L. Matrix reactions of silane and oxygen atoms. *Infrared*

- spectroscopic evidence for the silanol, silanone, and silanoic and silicic acid molecules. *J. Phys. Chem.* **89**, 3261–3268 (1985).
10. Binti Haji Musa, A., Malengier, B., Van Langenhove, L. & Stevens, C. The reliability of the newly developed bending tester for the measurement of flexural rigidity of textile materials. in *IOP Conference Series: Materials Science and Engineering* **254**, 142004 (2017).
 11. Inogamdjnov, D., Matsouka, D., Vassiliadis, S., Kizlaridis, I. & Daminov, A. Low Stress Shear Behaviour of Cotton Fabrics. *Fibers Polym.* **21**, 1355–1361 (2020).
 12. Chen, Q. *et al.* Development of tricot warp knitted fabrics with moisture management for casual shirt. *Fash. Text.* **9**, 4 (2022).
 13. Liu, R. *et al.* MXene-Coated Air-Permeable Pressure-Sensing Fabric for Smart Wear. *ACS Appl. Mater. Interfaces* **12**, 46446–46454 (2020).