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Formation of a crack-free, hybrid skin layer with tunable surface topography and improved gas permeation selectivity on elastomers using gel-liquid infiltration polymerization

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ABSTRACT Surface modifications of elastomers and gels are crucial for emerging applications such as soft robotics and flexible electronics, in large part because they provide a platform to control wettability, adhesion, and permeability. Current surface modification methods via ultraviolet-ozone (UVO) and/or O₂ plasma, atomic layer deposition (ALD), plasmas deposition, and chemical treatment impart a dense polymer or inorganic layer on the surface that is brittle and easy to fracture at low strain levels. This communication presents a new method, based on gel-liquid infiltration polymerization, to form hybrid skin layers atop elastomers. The method is unique in that it allows for control of the skin layer topography, with tunable feature sizes and aspect ratios as high as 1.8 without fracture. Unlike previous techniques, the skin layer formed here dramatically improves the barrier properties of the elastomer, while preserving skin layer flexibility. Moreover, the method is versatile and likely applicable to most interfacial polymerization systems and network polymers on flat and patterned surfaces.

INTRODUCTION

The flexibility of network polymers in their dry form (elastomer) and wet form (gels) has inspired applications in flexible electronics,¹⁻² soft robotics,³ optics,⁴ sensors,⁵ and microfluidics.⁶ Often, surfaces of the elastomers and gels must be modified to meet the requirements of the desired applications, from solvent retention to harvesting new functionality. For example, a hydrophobic polymer layer has been coated onto a proton exchange membrane (PEM) using plasma treatment.⁷ The coating layer cracked during the PEM hydration, but the crack openings progressively sealed during dehydration, which reduced the dehydration rate and improved the PEM performance at elevated temperatures. Besides continuous films, self-assembled colloidal particles can also be designed to form controlled cracks, useful for different applications.^{8,9}

Surfaces of polydimethylsiloxane (PDMS), one of the most frequently studied elastomers, can be modified using a variety of methods. UVO and O₂ plasma treatments result in a SiO_x-like skin layer.¹⁰ Under mechanical loading, such a stiff-on-compliant configuration leads to tunable surface features including micro lenses and,¹¹ more commonly, surface wrinkles.^{12, 13} Using periodic injection of tetraethyl orthosilicate (TEOS) and subsequent sol-gel deposition, a silica particle layer was deposited on the surface of PDMS particles, producing a series of unclonable micro-fingerprints.¹⁴ ALD-based sequential infiltration synthesis (SIS) was applied to impart metal oxides such as AlO_x within the PDMS surface layer, which improved triboelectric generation performance.¹⁵ However, the UVO-derived inorganic layers are brittle, while the SIS method is inefficient in terms of both throughput and chemical specificity.

Here, we report a simple and versatile method that can modify the surface of elastomers using a gel-liquid infiltration polymerization (GLIP). Using PDMS as a model system, the process

allowed formation of hybrid polyamide (PA)/PDMS skin layers, which sustained very large local strain without fracture, dramatically reduced the solvent/gas permeation, and improved gas selectivity.

RESULTS AND DISCUSSION

Figure 1a illustrates the GLIP process. A PDMS film, swollen with trimesoylchloride (TMC)/hexane solution, was placed within an aqueous solution containing 1, 3-phenylenediamine (MPD). Due to the asymmetry in solubility,¹⁶⁻¹⁷ MPD diffused into the PDMS gel and polymerized with the TMC, forming a PA/PDMS skin layer (Figure 1b). We chose the MPD/TMC system because the reaction is fast (within seconds to minutes depending on monomer concentration), and self-limiting (i.e., the skin layer serves as a barrier for further monomer diffusion and thus limits the skin layer thickness).¹⁸⁻²⁰ As the hexane evaporated, the PDMS substrate compressed and wrinkled the skin layer (Figure 1a). The maximum strain loading (ϵ_m) occurred when the skin layer had negligible solvent content, $\epsilon_m = (l_d - l_s) / l_s$, where l_d and l_s are the dimension of the PDMS at swollen and dry states, correspondingly. For equilibrium swollen PDMS (10:1), $\epsilon_m = -31.7\%$, consistent with literature report.²¹

Figure 1c shows the surface morphology of the PDMS (10:1) after reacting in 2 % MPD solution for different durations (TMC concentration was fixed at 0.2 % for all the samples). Topographic atomic force microscopy (AFM) images for all the samples are shown in Figures S1-S3, and geometry of the surface features are summarized in Table S1. The lateral feature size of the wrinkle-like structure increased from $\approx 0.6\ \mu\text{m}$ to $\approx 2\ \mu\text{m}$ as the reaction time increased from 15 s to 16 min, while the aspect ratio (height/ bottom width) of these features was similar, ranging from 0.5 to 0.6. For samples with 1 h and 2 h reaction, the surface topography became

more hierarchical, showing a combination of small ridges (width ≈ 400 nm to 500 nm and aspect ratios ≈ 0.7 to 1.0) and larger features (width ≈ 2 μ m to 2.5 μ m). After 12 h, the small ridges become the dominant morphology with aspect ratio ≈ 1.0 (Figure 1c).

The skin layer morphology can be controlled by the process parameters, as collectively demonstrated in Figure 2. Instead of equilibrium swelling, PDMS (10:1) was swollen in a TMC/hexane solution for 3 min and 10 min, to achieve $\epsilon_m = -10.7\%$ and $\epsilon_m = -20.0\%$, correspondingly. After reacting in 2 % MPD solution for 16 min, both samples displayed a creased skin layer with randomly oriented folds (Figure 2a, 2b), with 1 μ m to 3 μ m average distances between the neighboring folds. The folds of the sample with $\epsilon_m = -20.0\%$ (0.7 μ m to 1.5 μ m) was deeper than the sample with $\epsilon_m = -10.7\%$ (0.3 μ m to 0.9 μ m). Adjusting the crosslinking density of PDMS also leads to different degrees of swelling: for 20:1 and 40:1 curing ratios, ϵ_m increased to $\approx -40.0\%$ and $\approx -58.5\%$. After 16 min in 2 % MPD solution, the PDMS (20:1) sample displayed highly hierarchical surface structures (Figure 2c): deep wrinkles ≈ 2 μ m to 3 μ m wide and 0.7 μ m to 1.6 μ m deep, together with narrower (200 nm to 300 nm) and shallower (≈ 200 nm) wrinkles. For the PDMS (40:1) sample (Figure 2d), a ridge-like skin layer morphology with extremely high aspect ratio was observed: the width of the ridges was ≈ 2 μ m, but the height was above the measurement limits of the AFM. From scanning electron microscopy (SEM) images, the aspect ratio of the ridges can be up to ≈ 1.8 (see Figure S4 and following discussion in SI).

Achieving high-aspect ratio wrinkles and ridges using stiff-on-compliant configurations has been a challenge,²²⁻²⁵ because the stiff layers typically have low fracture strain. Under uniaxial compressive loading, the stiff layers often crack because of the tensile loading at the perpendicular direction, which can be minimized using bi-axial compression. Recently, using

incremental release of large pre-stretch^{26,27} or plastic deformation,²⁸ structures with aspect ratios as high as 1.5²⁴ and 2.0²² were fabricated. The method presented here yielded tunable skin layer morphology from hierarchical wrinkles to folds/ridges. According to Cao et al,²⁴ the aspect ratio of ridge-like structures is dictated by the pre-strain (ϵ_{pre}) as, $A_{ridge}/\lambda_{ridge} = 0.52 \epsilon_{pre} + 0.23$. Adopting this relationship, the PDMS (10:1) and (20:1) systems should have ϵ_{pre} of 45 % and 67 %, corresponding to predicted values of $A_{ridge}/\lambda_{ridge}$ of 0.46 and 0.58. As listed in Table S1, the dominant wrinkle morphologies have aspect ratio ranging from 0.5 - 1.1 for the PDMS (10:1) and PDMS (20:1) systems, which is comparable with the predict values. For the PDMS (40:1) system, ϵ_{pre} was ~ 142 %, corresponding to $A_{ridge}/\lambda_{ridge} = 0.98$, which is lower than the experimental estimation (up to 1.8). The discrepancy between the predicted values and our experimental data is likely resulting from both the fact that our skin layer is not a homogenous continuous film as used in the FEA modelling, and the uncertainty in defining λ_{ridge} for the less periodic structures such as the PDMS (40:1) system. Nevertheless, such rough skin-layers have large true surface area (A_t), as listed in Table S1. Specifically, A_t approaches maximum value of 214 %, and 277 % of the projected area (A_0) for the PDMS (10:1) and PDMS (20:1) systems. A_t for PDMS (40:1) was not determined, as the surface roughness was beyond the measurement limit of the AFM.

In traditional interfacial polymerization of TMC/MPD, both thickness and morphology of the PA layer can be controlled by monomer concentration and reaction time.^{16, 29} PA thickness as low as 8 nm was achieved with low MPD concentration, which lead to superior membrane performance.²⁰ This suggests that similar surface-layer control may be possible in GLIP. Figure 2e and 2f show the skin layers formed on PDMS (10:1) after 16 min reaction in 0.2 % and 0.02 % MPD solutions (samples with shorter reaction times are shown in Figure S3). For the 0.2 %

MPD systems, wrinkle-like structures were observed, with both the feature size and degree of hierarchy increasing with reaction time (Table S1). For the 0.02 % MPD system, however, the skin layer appeared distinctively different than that for both the 2 % and 0.2 % MPD systems. Specifically, perpendicular ridges with widths increasing from ≈ 160 nm at 15 s to 430 nm at 16 min and aspect ratios increasing from 0.6 to 1.0 were observed. In this low concentration system, the shrinkage-induced compressive strain was apparently highly localized.

In addition to topographically reconfiguring flat surfaces, the GLIP method can also modify pre-patterned PDMS surfaces, including micro lenses (Figure 2g, 2h), line-and-space gratings (Figure 2i, 2j), concentric rings (Figure 2k), and a custom “CU” logo (Figure 2l). For a given surface pattern, higher MPD concentrations and/or longer reaction times led to the formation of a thicker or stiffer skin layer, and thus larger instability-derived features. Unlike flat surfaces, the symmetry of the pre-patterns dictates the local strain state and thus the orientation of the wrinkles: randomly oriented short folds on lens (Figure 2g, 2h), folding along grating lines (Figure 2i, 2j), and a combination of both in the concentric ring (wide trenches vs. thin lines).

TMC/MPD derived PA layers on traditional interfacially-polymerized reverse osmosis (RO) membranes have a glass transition temperature, T_g , from 140 °C to 190 °C.³⁰ At room temperature, a dense PA layer is expected to be brittle, and will not survive the large-strain deformations observed in the ridges and folds. As such, the highly strained nature of the GLIP films indicates that the composition of the surface layer is not that of homogenous PA, but something far more ductile. Consistently, from the top-down and cross-sectional SEM images (Figure S5), no clear signs of phase separation between the PA and PDMS were evident.

To determine the composition and morphology of the GLIP surface layer, a series of chemical and mechanical characterizations were performed. X-ray photoelectron spectroscopy (XPS)

measurements revealed that the modified PDMS surfaces contained C, O, N, and Si, which consisted of 99 % of the total elements detected (Figure S6 for the survey scan and Table S2 for the summary). All sample surfaces showed an appreciable amount of Si, which allows estimation of the C % and O % contributed from the PDMS. Accordingly, the atomic percentage of C, O, N from PA (and residual monomers) can be extracted (see SI for detailed discussion), which further allows estimation of the mass concentration of PDMS in the top 5 nm to 10 nm layer (Table S2). For the PDMS (10:1) 2 % MPD system, the PDMS surface concentration decreased to 24.4 % after only 15 s reaction, and reached 12.2 % after 12 h. In contrast, for samples reacted in solutions with lower MPD concentrations, the PDMS concentration at the surface was high (70 % to 80 %) regardless of reaction time.

The O/N ratio of the PA provides a good estimation of the chemical composition of the PA: O/N =1 for a fully crosslinked network, and O/N =2 for linear chains.²⁰ For the 2 % MPD system, the O/N ratio decreased from 4.1 (15 s), to 1.1 (16 min), to 0.7 for longer reaction times (Table S2), all of which is consistent with MPD/TMC derived PA.^{20, 31} In contrast, for samples reacted with lower MPD concentrations (0.2 % and 0.02 %), the O/N ratios were higher than 2, indicating an excess of hydrolyzed TMC or insufficient MPD infiltration. As base-to-crosslinker ratio increased from 10:1 to 20:1 to 40:1, after 16 min in 2 % MPD solution, the O/N ratio of the PA-like materials increased from 1.1, to 6.7, to 38.7, suggesting an increase in the concentration of TMC-derivatives. Consequently, the PDMS concentration in the skin layer increased from 38.6 %, to 45.5 %, to 71.9 %. Water contact angle (CA, Table S2) of the PDMS samples also provides rough estimation of the surface chemistry, although it is convoluted with the effect of surface topography. Nevertheless, it appears that CA decreases with an increase in N at. %, from

$\approx 108.4^\circ$ to 114.7° for the pure PDMS,^{32, 33} to $\approx 60.6^\circ$ for 13 at. % N. The latter value was close to the CA of MPD/TMC derived PA ($\approx 51.2^\circ$ to 60.6°).²⁰

Whereas XPS and CA measurements are strongly surface-sensitive, they do not provide insight into the mechanics and morphology of the GLIP sample surface. Thus, contact resonance force microscopy (CR-FM) was used to probe the mechanical properties of the skin layers with high spatial resolution and sensitivity. In terms of elastic contact stiffness (Figure 3a), the samples are not readily differentiated from the PDMS reference until reaching the longer reaction durations of the 2 % MPD system. For the 12 h reaction duration, the contact stiffness is ≈ 3 times greater than for the pure PDMS. Nonetheless, the highest contact stiffness observed on infiltration polymerized samples is still a factor of 10 lower than a PS reference, suggesting the surface is not glassy as for traditional interfacially polymerized PA. When comparing $\tan \delta$ (Figure 3b), the damping of the modified PDMS surfaces is intermediate to both the PDMS and PS references, consistent with the model of a hybrid PA/PDMS material that is capable of extreme surface strain. Figure 3c plots the normalized (by pure PDMS) contact stiffness for several of the modified PDMS surfaces as a function of applied force. By controlling the applied force, we vary the depth of the stress field exerted beneath the AFM tip. If the hybrid layer were of similar or smaller dimensions than the stress field, a greater percentage of pure PDMS would enter the stress field as we press harder, resulting in a convergence (ratio = 1) of the infiltration polymerized properties and the bulk PDMS properties. For both 2 % MPD samples, slight divergence of the normalized stiffness ratio from 1 is observed. Only the 0.02 % MPD at 15 s sample shows convergence towards the PDMS value, however the trend is weak and could originate from epistemic uncertainties in the analysis. From Hertzian contact mechanics, we predict a stress field dominated by the top 30 nm to 50 nm of the sample for the lowest applied

force and 100 nm to 150 nm for the highest applied force, suggesting a hybrid layer thickness of > 100 nm. Beyond the average mechanical properties of the surface layer, CR-FM also provides insight into the mixing length scale of the PA/PDMS hybrid. When considering measurements obtained at all locations in the GLIP material, no data points exhibited a nanomechanical signature (i.e., a combination of stiffness and $\tan \delta$) equivalent to either the PDMS or PS references. Thus, the hybridization occurs at length scales smaller than the contact radius (i.e. < 20 nm).

The presence of a denser skin layer with large A_t would significantly improve the barrier properties of the PDMS for solvent permeation.³⁴ For example, Figure 3d shows that the hexane loss rate of GLIP PDMS (10:1, 2 % MPD, 16 min) ($t_{1/2} \approx 68.5$ min) is ≈ 10 times slower than that of the pure PDMS ($t_{1/2} \approx 6.2$ min) with identical geometry. The skin layer comprises highly cross-linked PA, resulting in the barrier properties.

We further demonstrate the barrier properties of the skin layer using gas permeation through the GLIP PDMS (10:1, 2 % MPD, 16 min). The GLIP PDMS showed significantly lower gas (H_2 , N_2 , CH_4 and CO_2) permeability (Figure 3e) than pure PDMS,³⁵ confirming the impact of the skin layer with highly cross-linked rigid networks and thus lower gas permeability. On the other hand, the skin layer significantly increased the H_2 /gas selectivity (Figure 3f) because of the enhanced size-sieving ability and diffusive selectivity in the rigid skin layer. For example, H_2/N_2 selectivity in the GLIP PDMS is 11, which is significantly higher than that in pure PDMS (= 2.0) or the Knudsen selectivity (= 3.7). Using a resistance-in-series model³⁶ (see SI for details), the estimated gas permeability and H_2 /gas selectivity in the skin layer is presented in Figure 3f. The GLIP skin layer has almost four orders of magnitude lower permeability and dramatically higher H_2 /gas selectivity than the underlying PDMS. Although further studies will be needed to

thoroughly quantify the gas transport properties of the skin layer, the demonstration clearly reveals that the presence of the skin layer, even modified with 0.2 % MPD concentration, can significantly reduce the permeation and enhance the gas selectivity.

CONCLUSION

In conclusion, we report a versatile method to modify the surface of PDMS, by using gel-liquid infiltration polymerization. Because of both the self-limiting nature of the TMC/MPD reaction and the network constraints for nanogel diffusion, PA formed only near the PDMS surface, yielding a crack-free hybrid skin layer. The skin layers have low solvent solubility and are stiffer than the bulk PDMS, which leads to the formation of a series of hierarchical surface features on the dried PDMS with aspect ratio as high as 1.8 without fracture. We demonstrated that the morphology and properties of the skin layers can be controlled by adjusting both the process conditions and substrates topography, and that the skin layers significantly reduce the solvent/gas permeation and improve the gas selectivity. Different from the reactive infusion process where a reactive silane diffuse and covalently bounded to the network,³⁷ the infiltrated polyamide is physically fused with the PDMS network within the skin layer. Thus, the GLIP processes is extremely versatile: the infiltrated polymers can be selected from a broad range of interfacial polymerization systems,³⁸ and the substrates can be any polymer networks. Recently, studies have shown that imparting surface topography on separation membranes can enhance separation performances, from increasing permeation³⁹ to improving antifouling performances due to the topography-enhanced back diffusion.^{40,41} We envision that the approach reported here can be used to improve different separation applications from gas separation to pervaporation.

EXPERIMENTAL SECTION

Infiltration polymerization process PDMS films (Sylgard 184, Dow Corning) with base-to-curing-agent ratio of 10:1, 20:1 and 40:1 were cured at 80 °C for 2 hours, and were cut into 8 mm × 8 mm pieces ($\approx$ 2 mm thick) for the subsequent experiments. PDMS samples were swollen in a hexane (Fisher Scientific) solution containing 0.2 % TMC (99 %) for different durations, followed by reaction in an aqueous solution containing MPD (0.02 %, 0.2 %, or 2 %), 2 % triethylamine (TEA), and 4 % (1S)-(+)-10-camphor-10-sulfonic acid (CSA) for different durations.^{19, 42} MPD, TEA, and CSA were purchased from MilliporeSigma, and used as received and all concentrations were mass percentage unless otherwise noted. After the reaction, the PDMS samples were rinsed with DI water and dried under a chemical hood for 24 h. In addition to flat surface, PDMS (10:1) with three types of surface patterns were examined: line-and-space gratings, concentric rings, and micro lenses. The gratings and concentric rings were replicated by curing PDMS onto Si templates, which were fabricated with standard photolithography.^{43, 44} The PDMS micro lenses were replicated from PS templates, which were fabricated using a breath-figure-templated self-assembly (BFTA) method.⁴⁵

Characterization of skin layer Field emission SEM (JEOL JSM-7401F) was used to characterize both the surface and cross-sections of the modified PDMS. All the samples were coated with a $\approx$ 5 nm gold layer before SEM measurements. Quantitative analysis of the surface topography was carried out with an AFM (DI 3100, Bruker). For each sample, measurements at three randomly selected locations across the surface were carried out. A second AFM (Cypher, Asylum Research) was used to perform viscoelastic nanomechanical characterization of the sample surface with CR-FM,⁴⁶ applying a 3 N/m cantilever with a specially fabricated hemispherical tip of 60 nm nominal radius (HSC 60, Team Nanotec). The 3rd eigenmode free

resonance frequencies and quality factors of the cantilever were compared to corresponding values of the cantilever in contact with the sample to determine the effective loss tangent and contact stiffness of the sample surface.^{46, 47} At least 15 locations on each sample were probed with an applied force of $35 \text{ nN} \pm 5 \text{ nN}$. A subset of samples representing expected property extremes was characterized at a range of forces from $35 \text{ nN} \pm 3.5 \text{ nN}$ to $565 \text{ nN} \pm 57 \text{ nN}$.

Surface elemental analyses were carried out using XPS with an Axis Ultra DLD Imaging Spectrophotometer (Kratos Analytical) and monochromatic Al K α X-rays (8 mA; 13 kV). Emitted photoelectrons were collected along the surface normal over a field of view defined by a hybrid lens and a slot aperture (over 90 % of signal from a $0.94 \text{ mm} \times 2.25 \text{ mm}$ area),⁴⁸ with the exception of the native PDMS films which were collected using FOV1 lens and a $110 \text{ }\mu\text{m}$ aperture. For each specimen, high resolution spectra were acquired for the O 1s, N 1s, C 1s, Si 2p, Cl 2p, and S 2p. All spectra were energy corrected by adjusting the Si 2p peak position to 102.1 eV, a value comparable with literature references for PDMS.⁴⁹ All spectra were fit with Shirley backgrounds and peak areas were corrected using elemental relative sensitivity factors from the manufacturer. All values reported are the average value and standard deviation from 4 measurements at spots separated by 1 mm to 2 mm.

Water CA measurements were obtained with a custom-built image system (Fastcam SA4, Photron), with a $2 \text{ }\mu\text{L}$ DI-water droplet. For each sample, at least three repeated measurements were carried out, and the average values are reported here. Pure gas permeability of H₂, N₂, CH₄ and CO₂ in PDMS (10: 1) in 0.2 % MPD for 16 min sample was determined using a constant-volume and variable-pressure apparatus at 35 °C.^{50, 51} The PDMS films used have a thickness of $\approx 100 \text{ }\mu\text{m}$ and an active area of 0.37 cm^2 . The feed pressure was varied at 50 psig and 100 psig, while the downstream was kept under vacuum, and the steady-state rate of pressure increase in

the fixed downstream volume was recorded and used to calculate gas permeability. Permeability of the film to gas component has units of Barrer ($1 \text{ Barrer} = 1 \times 10^{-10} \text{ cm}^3 \cdot (\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cm} \cdot \text{Hg}^{-1}$).

FIGURES

Figure 1. (a) Illustration of infiltration polymerization process, and photographs of PDMS samples at each step. (b) Mechanism of the PA/PDMS skin layer formation. (c) SEM images of the PDMS (10:1) surface after the infiltration polymerization process in 2% MPD solution for different durations as labelled. The scale bars in the main figure and the inset apply to all the images.

Figure 2. SEM images of the skin layers formed after 16 min reaction in (a-d) 2 %, (e) 0.2 %, and (f) 0.02 % MPD solution: (a) and (b) are PDMS (10:1) with 3 min and 10 min pre-swelling in TMC/hexane solution, respectively; (c) and (d) are PDMS (20:1) and PDMS (40:1) after equilibrium swelling in TMC/hexane solution; (e) and (f) are PDMS (10:1) with equilibrium swelling in TMC/hexane. (g-l) are SEM images of the patterned PDMS (10:1) after reaction under conditions as labelled: (g-h) micro-lens, (i-j) line-and-space gratings, (k) concentric ring, and (l) a “CU” logo. The scale bars in the insets for (a-j) correspond to a length of 5 μm , and 10 μm in (k).

Figure 3. (a) and (b) show the contact stiffness and loss tangent as a function of reaction duration. Horizontal bars represent properties of bulk references (PS and PDMS). (c) shows the contact stiffness of the modified surfaces, normalized by the value of bulk PDMS, as a function of applied force. (d) Solvent mass, normalized by the initial value, in the PDMS as a function of drying time for pure and modified PDMS. Comparison of (e) pure gas permeability and (f) H₂/gas selectivity in pure PDMS (data from ref.³⁵) and PDMS (10:1) 0.2 % MPD 16 min and the estimated PA-filled skin layer.

ASSOCIATED CONTENT

Supporting Information (docx). Contains additional experimental details and analysis, including: conditions for all the samples prepared; topographic AFM images of the surface and corresponding analysis; Cross-sectional SEM of the skin layer; XPS analysis (survey scans and detailed elemental analysis); analysis of gas permeation.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Table of Contents

Supporting Information

Formation of a crack-free, hybrid skin layer with tunable surface topography and improved gas permeation selectivity on elastomers using gel-liquid infiltration polymerization

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1. Table S1. Summary of the topographic features on the modified PDMS surfaces from AFM measurements

PDMS	MPD (%)	Reaction time (s)	Larger feature (1 st order)		Smaller feature (2 nd order)		A_t/A_0 ^a (×100%)
			Lateral (μm)	aspect ratio	Lateral (μm)	aspect ratio	
10:1	2	15	0.7±0.1	0.6	---	---	178.3±19.4
		60	0.8±0.1	0.6	---	---	179.5±10.4
		960	2.0±0.2	0.5	0.5±0.1	0.7	209.2±31.3
		3600	2.2±0.3	0.3	0.5±0.1	1.0	216.7±20.6
		7200	---	---	0.6±0.1	0.9	217.2±9.2
		43200	---	---	0.7±0.1	0.7	210.0±10.8
	0.2	15	---	---	0.1±0.0	0.5	143.3±17.9
20:1	0.2	60	0.7±0.1	0.3	0.3±0.1	0.6	152.0±1.8
		960	1.4±0.2	0.3	0.3±0.1	0.6	169.9±0.4
		960	0.4±0.2	1.1	0.3±0.1	0.6	204.6±18.4
	0.02	15	0.2±0.0	1.0	0.2±0.0	0.6	144.1±6.9
		60	0.2±0.1	1.1	0.3±0.1	0.5	186.0±9.3
		960	0.4±0.2	1.1	0.3±0.1	0.6	204.6±18.4
	2%	960	2.6±0.2	0.7	0.3±0.1	0.7	270±21.5

^a A_t and A_0 is the true surface area and the projected surface area for the skin layers, obtained from AFM scan. Maximum value of A_t , corresponding to the surface area of the swollen PDMS, was 214%, 277%, and 581%, for PDMS with 10:1, 20:1, and 40:1.

2. The topographic AFM images of the PDMS surfaces after infiltration polymerization

Figure S1. Surfaces of PDMS (10:1) in 2% MPD with different reaction time: (a) 15 s, (b) 1 min, (c) 16 min, (d) 1 h, (e) 2 h and (f) 12 h. All images are $20\ \mu\text{m} \times 20\ \mu\text{m}$, and the z-scale bar on the right corresponds to a range of 0 nm - 2000 nm.

Figure S2. Surfaces of PDMS (10:1) with (a) 3 min and (b) 10 min swelling in TMC/hexane solution, followed by reaction in 2% MPD aqueous solution for 16 min. (c) Surface of PDMS (20:1) with overnight swelling in TMC/hexane solution, followed by reaction in 2% MPD aqueous solution for 16 min. All images are $20\ \mu\text{m} \times 20\ \mu\text{m}$. The z-scale bar on the right corresponds to a range of 0 nm - 3000 nm.

Figure S3. Surfaces of PDMS (10:1) after reaction in 0.2 % MPD solution for (a) 15s, (b) 1 min, and (c) 16 min. Correspondingly, (d), (e), (f) represent the PDMS (10:1) surface after reaction in 0.02 % MPD solution for 15s, 1 min, and 16 min. All images are $20\ \mu\text{m} \times 20\ \mu\text{m}$. The z-scale bar on the right corresponds to a range of 0 nm - 2000 nm.

3. Morphology and cross-sections PDMS (40:1) sample

Figure S4. SEM images of the PDMS (40:1) in 2 % MPD for 16 min: Top-down view with (a) low and (b) high magnification; (c) Cross-sectional view of the sample fractured in liquid nitrogen.

Note that there is discrepancy between our definition of aspect ratio (height/width) with the one used in the wrinkling community, where it is defined as the ratio between the amplitude and wavelength (or characteristic length) of the wrinkle/ridges. For the PDMS (40:1) sample shown above (Fig. S4a), the characteristic wavelength is quite challenging to define. Using the height and width defined in the figures, the aspect ratio was ~ 6 . Nevertheless, to be consistent with literature, we adopt the definition of aspect ratio used in wrinkling literature, using the bottom width (Fig. S4c). As a result, the aspect ratio of the PDMS (40:1) sample was quantified as “up to 1.8” in the paper.

4. Cross-sectional SEM of PDMS (40:1) in 2 % MPD for 16 min

Figure S5. Cross-sectional SEM image of a) PDMS (10: 1) in 2% MPD for 16 min, b) is the higher resolution view of a). c)PDMS (40: 1) in 2 % MPD for 16 min. All samples fractured at room temperature.

5. XPS measurement and composition analysis

Figure S6. XPS survey scan spectra of PDMS surfaces after infiltration polymerization process for different times and different MPD concentrations.

Table S2. Summary of XPS and contact angle measurements for the modified PDMS surfaces.

PDMS	MPD (%)	Reaction time (s)	Atomic percentage from XPS ^a					O/N ratio ^c	PDMS % ^d	Contact angle (°)
			C (%)	N (%)	O (%)	Si (%)	Cl ^b (%)			
10:1	---	---	48.5±0.3	0	29.2±0.3	22.3±0	0	---	100%	108.4±1.9
	2	15	62.9±0.3	5.1±0.1	26.9±0.1	4.5±0.2	0.5±0.3	4.1	24.4±0.1	101.3±7.1
		960	63.6±1.4	9.1±0.1	19.2±0.9	7.2±0.9	0.8±1.6	1.1	38.6±0.2	84.2±5.9
		3600	65.1±3.3	11.3±0.2	16.4±1.3	6.1±2.6	1.0±2.3	0.7	33.4±0.4	76.7±1.2
		7200	73.0±2.6	13.0±0.2	9.9±0.8	2.7±2.0	1.2±1.5	0.5	15.7±0.1	59.4±1.9
		43200	72.5±1.9	12.7±0.2	11.4±1.2	2.1±1.6	0.7±1.1	0.7	12.2±0.1	82.7±2.1
	0.2	15	55.4±0.5	1.6±0.1	27.6±0.1	15.3±0.1	0.1±0.5	4.7	73.6±0.0	NA
		900	54.4±0.2	1.1±0.0	28.4±0.2	16.2±0.4	0.0±0.7	6.8	77.2±0.0	NA
	0.02	15	57.0±0.3	1.8±0.0	27.2±0.1	14.0±0.4	0.1±0.5	5.1	68.3±0.0	105.3±3.3
		240	56.5±0.6	1.6±0.1	26.7±0.1	15.0±0.3	0.1±0.8	4.4	72.9±0.0	105.5±4.6
20:1	---	---	48.5±0.4	0	29.4±0.3	22.1±0.1	0	---	100%	109.9±2.0
	2	960	60.9±2.4	2.4±0.6	27.6±0.0	8.8±0.6	0.3±2.4	6.7	45.5±0.8	112.6±8.4
	---	---	48.5±0.5	0	29.2±0.1	22.3±0.4	0	---	100%	114.7±5.4
40:1	2	960	56.1±3.1	0.2±0.1	26.6±0.5	14.4±0.6	2.7±3.6	38.7	71.9±1.6	133.3±5.6

^a The listed values are average from four measurements at different spots. Most of the standard deviation is less than 0.5% and not included here for clarity.

^b Residual Cl from either unreacted acyl chloride groups or HCl (reaction byproduct) was $\approx 1\%$ or less, and neglected in the following analysis.

^c The O/N ratio for the polymers after subtraction O from PDMS.

^d The mass of hydrogen in both PDMS and the polyamide formed was not accounted. The error bars are calculated based on error propagation from the C, N, O, and Si data in this table.

6. Estimation of PDMS wt% in the skin layer using XPS measurements

From XPS measurements of native PDMS with different curing ratio (Table S2), the atomic ratio among C, O, and Si is 2.2/1.3/1, suggesting a chemical formula of $C_{2.2}O_{1.3}Si$ (neglecting H). For PDMS modified with infiltration polymerization, Si atomic content from the XPS measurements exclusively comes from PDMS, and N exclusively comes from the infiltrated polyamide. According to $C_{2.2}O_{1.3}Si$, the atomic content for C and O from PDMS can thus be calculated as 2.2 times and 1.3 times of atomic content of Si. Therefore, the following calculations were carried out:

- (1) The O/N ratio in the infiltrated polyamide (Table S2): the atomic content of the O in polyamide equals the total O content from XPS measurements subtracts the O content from PDMS (1.3 times of Si atomic content). N atomic content is directly measured from XPS.
- (2) The PDMS weight percentage in the skin layer of the modified PDMS:

$$\text{PDMS percentage\%} = \frac{12 \times 2.2 \times \%Si + 16 \times 1.3 \times \%Si + 28 \times \%Si}{12 \times \%C + 16 \times \%O + 28 \times \%Si + 14 \times \%N + 35.45 \times \%Cl} \% \quad (1)$$

Note that H-content is neglected for the calculation, since it is not quantified from XPS.

7. Analysis of gas permeability of the skin layer

The gas transport properties in the polyamide-filled skin layer can be modeled using the following equation, assuming there is a skin layer on each side of the PDMS film (because of the processing method used):

$$\frac{l}{P} = \frac{l_{PDMS}}{P_{PDMS}} + \frac{2l_{skin}}{P_{skin}} \quad (2)$$

where l is the thickness (cm), P is the gas permeability, and the subscript of *PDMS* and *skin layer* indicates the properties for the PDMS layer, and the skin layer, respectively. Since the skin layer (< 500 nm) is much thinner than the PDMS layer (≈ 100 μ m), the value of l is essentially the same as l_{PDMS} . The estimated skin layer permeability is plotted in Figure 3f of the main text.