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## Rapid photothermal curing of PDMS on paper

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The desire for rapid curing of thermally-cured thermoset polymers directly on thermally-sensitive substrates, such as textiles, presents a dilemma: rapid curing requires high temperatures, but low temperatures are needed to preserve the properties of the substrate. In this manuscript, we test the ability of photothermal curing of polydimethylsiloxane (PDMS) bearing 0.5 wt% carbon black to cure PDMS on a thermally sensitive substrate (paper). Using differential scanning calorimetry and thermogravimetric analysis, we find that photothermal curing using  $\sim 18 \text{ W cm}^{-2}$  of 808 nm light is able to cure PDMS on paper to the same extent as curing in a furnace at 200 °C, but in 1/60 the time. Furthermore, examining the color of the paper as well as its Young's modulus, toughness, and strength, we find that treatment in the oven changes these properties significantly, while photothermal curing leaves them statistically unchanged. In total, we demonstrate that photothermal heating is one way to realize curing of PDMS on thermally-sensitive substrates, while preserving the properties of the substrate.

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### 1. Introduction

Thermally-cured thermoset polymers coatings, such as polydimethylsiloxane (PDMS), are widely used to add functionality to surfaces and interfaces.<sup>1–3</sup> These coatings are used to improve chemical resistance, physical protection, anti-biofouling capabilities, anti-drag behaviors, anti-reflective properties, and can even offer band pass/rejection functionalities.<sup>4</sup> For these reasons, thermoset coatings can be found on a wide variety of materials, from metals to plastics.

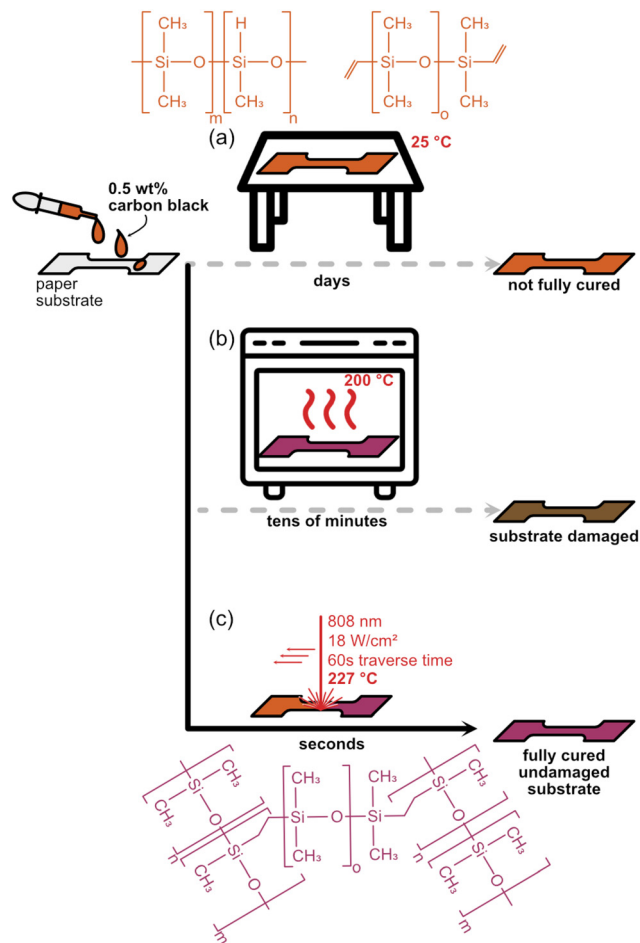
It is not uncommon for thermally-cured thermosets to require days to cure under ambient conditions. Popular formulations of PDMS can take up to 48 hours to set and, for this reason, it is common to supply additional heat to shorten curing times to minutes. However, there are classes of materials that would benefit from the application of coatings like PDMS, but which also undergo undesirable and irreversible changes at the high temperatures required for rapid curing; one such class is textiles. For these thermally sensitive materials, which constitute clothing and paper products, properties such as color and physical strength can be drastically altered under high temperatures. In the extreme limit, these materials will pyrolyze or combust,<sup>5</sup> radically changing their chemical identity. Thus, when attempting to coat textiles with thermally-cured thermosets, there is a tension between the desire to increase the speed of curing and the need to preserve the underlying textile's properties. Often, it is the need to preserve properties that wins out, and curing must be done at

a temperature low enough that the time-to-cure becomes impractical for many applications. Thus, it is imperative to find a way to supply heat to cure coatings while preserving the chemical and mechanical properties of the underlying thermally sensitive substrates.

Photothermal curing of thermoset polymers, driven by photothermal heating of nanoscale agents, offers a possible solution to the above problem. At its basic level, this approach involves selecting a nanoscale material that can absorb light energy and convert it to thermal energy, such as metallic nanoparticles or carbon black. Dispersing these photothermal agents in a reaction medium and then shining light on the material produces heat that can be intense (*i.e.*, thousands of degrees), tightly localized (*i.e.*, nanometers), and readily controlled *via* application of light.<sup>6–8</sup> The heating produced in this manner is capable of driving a wide variety of chemical reactions, such as the deposition of solid state materials,<sup>9</sup> small molecule reactions,<sup>10–13</sup> degradation of polymers,<sup>14–16</sup> and curing of polymers.<sup>17–19</sup> The last case includes the rapid curing of PDMS.<sup>20–22</sup> In many of these cases, it has been shown that photothermal heating can produce large local changes of temperatures that increase the rate of reactions by as much as a billion-fold while also limiting bulk-scale heating to as few as tens of degrees.<sup>17,21</sup> Taken together, these observations suggest that this approach could be used for the rapid curing of thermosetting polymers on thermally-sensitive substrates, while preserving the substrate's properties.

Herein, we report on our efforts to coat a textile (paper) with a thermosetting polymer (PDMS) using carbon black as the photothermal agent and a CW laser as the light source. The process is illustrated in Fig. 1. Paper was selected as a





**Fig. 1** A schematic representation of the key results of the study. A polymer containing a small amount of carbon black is added to paper and then cured under three conditions. (a) Under ambient conditions, the polymer takes several days to 'cure'. (b) Heating the polymer to the maximum manufacturer recommended temperature cures the polymer in an hour, but results in significant changes to the paper substrate. (c) Photothermally curing the polymer enables curing within a minute, and does not damage the underlying thermally sensitive substrate.

textile because it has strongly temperature-sensitive properties. For instance, the color of paper is often a critical consideration in its use, but paper can readily experience yellowing or browning within the range of curing temperatures recommended by the manufacture for common commercial formulations of PDMS. Stora Enso paper, specifically, was selected because a common step in its commercial preparation is to coat it with various polymers, for example, to provide waterproofing to disposable coffee cups. For that specific application, thermoplastic polyethylene is commonly used.<sup>23</sup> However, polyethylene has a lower LD50 value ( $3.4 \text{ g kg}^{-1}$ )<sup>24</sup> our chosen polymer (polydimethylsiloxane, LD50 =  $28 \text{ g kg}^{-1}$ )<sup>25</sup> and is less hemocompatible and more inflammatory.<sup>26</sup> PDMS was selected because it is often used to provide water-proofing ability, increase hydrophobicity of substrates, and is biocompatible.<sup>27,28</sup> Carbon black was selected because it is an inexpensive material known to be an effective photothermal

agent,<sup>22</sup> is biocompatible,<sup>29</sup> and has no current restriction for use in food-contact polymers, according to the USA Food and Drug administration (regulation 21 CFR § 178.3297).

Using our photothermal approach, we find that we are able to coat the paper with PDMS and fully cure it (as measured by differential scanning calorimetry), all while retaining the attractive features of both the paper and the coating—namely mechanical strength, hydrophobicity, and coloration. In contrast, a comparable cure of the paper's PDMS coating using conventional oven-curing significantly altered these properties and required at least 60× longer to cure, while 'curing' at room temperature avoided discoloration, but took many thousands of times longer (Fig. 1) and did not cure to the same extent. In total, this work demonstrates that photothermal heating is a viable approach to driving reactions with considerable barriers at a rapid rate even on substrates that are thermally-sensitive. We note that, while photothermally curing PDMS with carbon black has been studied in-depth,<sup>20–22</sup> the purpose of this study was to demonstrate that this process could be applied even on thermally-sensitive materials without deleterious effects.

## 2. Methods

Stora Enso coffee cup paper was coated with a composite of PDMS Sylgard 184 Silicone Elastomer Kit and Carbon Black (CB) Vulcan XC 72R nanoparticles (20–50 nm in size). A 0.5 wt%. CB stock solution made in-lab was used as a standard for the samples including CB. To prepare the formulation, a 1000 : 1 mixture of PDMS pre-polymer to CB was made first. Next, the Sylgard kit components were mixed in a 10 : 1 pre-polymer to curing agent ratio, producing the final carbon black PDMS (CB-PDMS) dispersion. The mixture was stirred vigorously by hand for 2 minutes to ensure even mixing. The stirred mixture was vacuum treated at room temperature (20 °C) for 5 to 10 minutes at 0.25 atm in order to remove gas bubbles. To coat the paper, a plastic spatula was used to smooth a layer of the CB-PDMS coating on the top of each coated sample for heat treatment.

Photothermal-coated samples were cured with an OsTech 80 W 28FF 808 nm CW laser with power densities ranging between  $17.4 \text{ W cm}^{-2}$  and  $18.7 \text{ W cm}^{-2}$ . The beam width was collimated to 1 cm to encompass the width of the samples. To irradiate the length of the samples, they were placed atop a mobile platform and then slid through the laser beam at a translation speed of approximately  $1 \text{ cm s}^{-1}$ . We noticed that the sample underwent a change in the glossy appearance at the sample surface that correlated with complete curing, which we later verified using differential scanning calorimetry. Thus, we were able to use this change in appearance to judge if a sample was likely fully cured (confirmed using differential scanning calorimetry) during the photothermal treatment. Curing was accomplished in under 1 minute; times longer than 2 minutes resulted in visible smoking and charred samples while times under 10 seconds did not yield visible changes. A Thermo Scientific Lindberg Blue M furnace,



referred to as an “oven” throughout this paper, was additionally used to cure samples. Samples were cured in the oven at 200 °C for 60 minutes and then removed to cool to room temperature.

For differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), photothermal-coated, oven-coated, and uncoated paper were heated from room temperature to 500 °C at 10 °C min<sup>-1</sup>. The DSC samples were run in nitrogen gas while the TGA samples were run in air.

For contact angle testing, a sample 1 × 1 cm of the paper was pinned to cardboard to immobilize it, and then a 5 μL droplet of water was placed onto the surface with a micropipette and photographed for data analysis. ImageJ software and the Contact Angle plugin were used to determine the angle between the droplet and the surface for each sample *via* baseline fitting and automated shaping.

For mechanical property testing, samples were placed in a MTS Criterion Model 43 universal tensile load frame. Samples were dotted with black marker in order to track stretching and percent strain increase. Paper was cut into a dog bone shape, with a narrower body for breaking at a known cross-sectional area and wider edges for gripping. A 1 kN load cell with two clamps within the instrument grabbed on to the top and bottom parts of the paper to pull apart the paper at a constant strain rate of 1 mm min<sup>-1</sup>.

### 3. Results

To examine the effects of photothermal curing of PDMS on paper and to compare photothermal curing to more conventional curing methods, we examined the properties of paper, treated under six conditions:

1. **Unheated-coated paper**, for which PDMS was applied and then left to cure under ambient conditions (room temperature and fluorescent lighting) for 48 hours. This follows manufacture recommendations for curing at room temperature. This condition allowed us to compare the properties of paper that was coated using heat (photothermal or oven) to increase the rate of reaction.

2. **Uncoated paper**, for which no treatment was applied and which serves as the baseline behavior of the paper.

3. **Oven-coated paper**, for which PDMS was applied and then cured in an oven at 200 °C for 1 hour. This condition mimics what one might use to maximize the rate of curing using conventional approaches, while also staying within the bounds of the manufacturer's recommendations for PDMS (lower temperatures are examined in section 4).

4. **Oven-uncoated paper**, for which no PDMS was applied, but samples were still placed in an oven at 200 °C for 1 hour. This condition allows us to isolate the effects of the oven from those of heating a coated sample.

5. **Photothermal-coated paper**, for which PDMS was applied and cured photothermally by passing the sample under ~17 W cm<sup>-2</sup> of laser light at a translation rate of ~1 cm s<sup>-1</sup>. The length of time required to cure is dependent on the size of the

sample, because the sample must be translated under the sample. For tensile coupons, the total irradiation was 60 seconds. More details on the kinetics of curing for PDMS under similar conditions can be found in a recent publication.<sup>22</sup>

6. **Photothermal-uncoated paper**, for which no PDMS was applied, but were still exposed to the same laser treatment used for the photothermal curing. This condition allows us to isolate the effects of the laser from those of curing the polymer, as well as examine the direct effects of the laser irradiation of the substrate.

Samples for each condition were generated as detailed in the Experimental section.

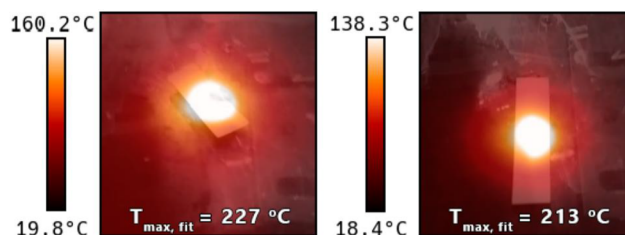
#### 3.1. Thermal images

In order to further verify that exposure to the laser light can produce significant heating of the polymer and paper, we acquired thermal images of samples that had the pre-polymer or were uncoated during exposure to laser irradiation. These images are shown in Fig. 2.

In inspecting these images, one can see that the coated paper reaches a higher temperature than the uncoated sample. This is an expected result, given that the coated sample bears pre-polymer with the photothermal agent. However, the thermal camera used cannot spatially resolve the true maximum temperature from a clipped signal, as shown in Fig. S9. Thus, the temperatures directly observed in Fig. 2 represent the *lower* bounds for the maximum temperature. We attempted to estimate the true maximum by fitting the observed profiles to a Gaussian profile, which prior simulations<sup>7,22</sup> suggest is appropriate. These fits suggest maximum temperatures of 227 ± 6 °C for the coated paper and 213 ± 10 °C for the uncoated paper. The results of this fitting can be seen in Fig. S9, and an explanation of the fitting accompanies that figure. These temperatures are reported in Fig. 2 as  $T_{\text{max,fit}}$ . From this analysis, we find that laser irradiation produces significant heating of the sample, even when the CB-PDMS composite is not present.

#### 3.2. Differential scanning calorimetry (DSC)

We used DSC to verify that photothermal heating could cure a film to the same extent as those cured in an oven. While prior



**Fig. 2** Thermal images of coated paper (left) and uncoated paper (right). Note that the color maps have different temperature scales between these two images yet share the same colors for their minimum and maximum temperatures. Labeled on the images are the maximum temperatures estimated by fitting the thermal profiles (see Fig. S9).



work on photothermally curing PDMS employed IR to directly track the progress of the reaction,<sup>20–22</sup> we have found that the use of CB makes use of ATR challenging and our use of textiles prevents the use of transmission IR.

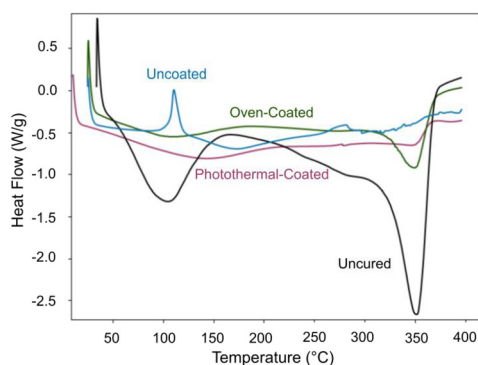
Fig. 3 shows four DSC traces, all normalized to the mass of paper present in the sample. The four samples include oven-coated samples (green) and photothermal-coated (dark magenta) treatments, as well as uncoated paper (blue) and paper where PDMS was applied but not cured prior to acquiring the DSC trace (black). Samples normalized to the amount of PDMS can be found in Fig. S2. A baseline of pure elastomer was run to compare to polymer-coated paper, which is illustrated in Fig. S3.

The extent of curing between the oven-coated and photothermal-coated conditions can be understood by comparing them to the sample with uncured PDMS (black). This trace contains two major features: exothermic events at roughly 100 °C and 350 °C. The first of these is associated with the normal curing of PDMS. We are uncertain as to the nature of the higher temperature feature. While it is tempting to ascribe this to pyrolysis of the textile, we also note that this feature is absent from the uncoated sample (blue) and so we conclude the feature is associated with PDMS composite. We note that pure PDMS also contains a similar feature, supporting the assignment that it is due to PDMS. While PDMS has high thermal stability at high temperatures, applied heat begins to initially break cross-linking before the bulk degradation process.<sup>30</sup>

When comparing the oven-coated (green) and photothermal-coated (dark magenta) samples to the uncured sample, we find that the oven-coated sample contains noticeable features at both 100 °C and 350 °C, while these features are either absent or nearly absent for the photothermal-coated samples. From this observation, we conclude that the photothermal-treated sample appears to be more cured than the sample heated in an oven.

### 3.3. Thermogravimetric analysis (TGA)

To assess the amount of PDMS present after curing, and to determine if this PDMS shows similar thermal behaviors, we

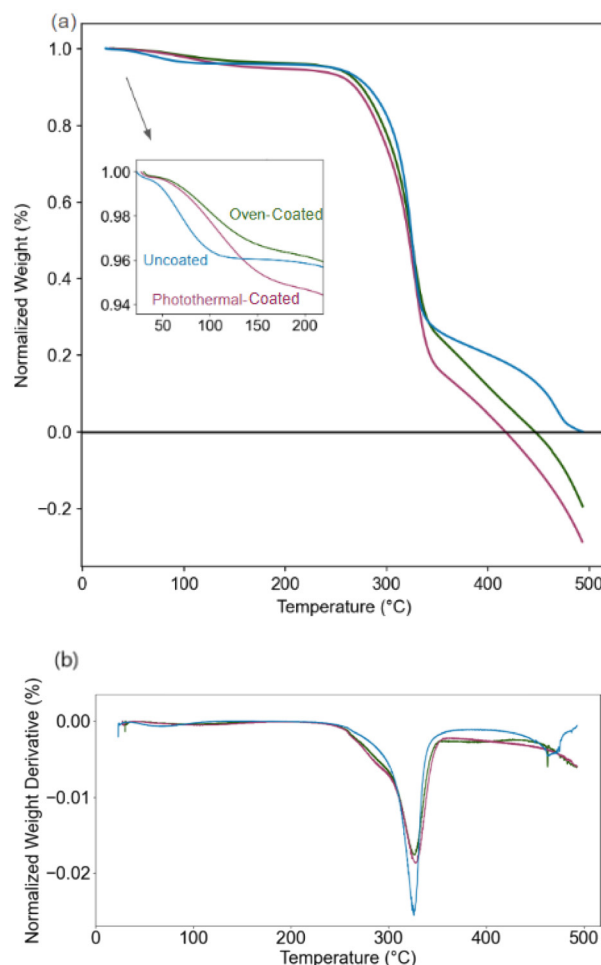


**Fig. 3** DSC data for photothermal-coated (dark magenta), oven-coated (green), uncured (black), and uncoated (blue) paper samples. All curves were normalized to the mass of the paper present in the sample.

turned to TGA. Fig. 4 shows the TGA of three samples: the photothermal-coated PDMS (dark magenta), oven-coated PDMS (green), and uncoated paper (blue). The traces shown are normalized to the mass of the paper, so that a weight of 0 indicates loss of mass equal to the mass of the paper.

Up until 340 °C, the traces are remarkably similar between these treatments. All samples show a small mass loss below 200 °C, which we ascribe to loss of water. We also observe a mass loss event at 350 °C. Based on prior work, we assign this mass loss to the thermal decomposition of the paper.<sup>31</sup> Beyond this temperature, the samples bearing PDMS coatings continue to decrease in mass, eventually creating mass losses greater than the mass of the paper, indicating that some PDMS decomposition must be occurring. This is expected, as thermal degradation of PDMS is known to occur between 400 °C and 600 °C.<sup>32</sup>

Perhaps the most salient feature of these traces is that the behavior of the oven-coated and photothermal-coated samples



**Fig. 4** Results of TGA measurements on uncoated (blue), oven-coated (green), and photothermal-coated (dark magenta) samples. (a) TGA traces for each sample, normalized to the amount of paper present. The uncoated sample (blue) is considered 100% paper. The inset focuses on the region below 200 °C. (b) Derivative plot of the traces shown in (a).





is quite similar. Indeed, plotting the differential TGA (Fig. 4b) reveals that the onset temperatures for the decomposition events are quite similar between the two curing modalities, while both differ slightly from the uncoated paper. Thus, from TGA we conclude that curing of PDMS on the paper alters the thermal decomposition slightly, but that photothermal curing does not lead to different behavior from oven curing.

### 3.4. Contact angle tests

To test if photothermal-coated polymers retained the same hydrophobicity as conventional oven-coated samples, we performed contact angle measurements on photothermal-coated and oven-coated samples. Fig. 5 reports the average contact angle and standard errors across five measurements each made on different samples from photothermal-coated, oven-coated, and uncoated conditions.

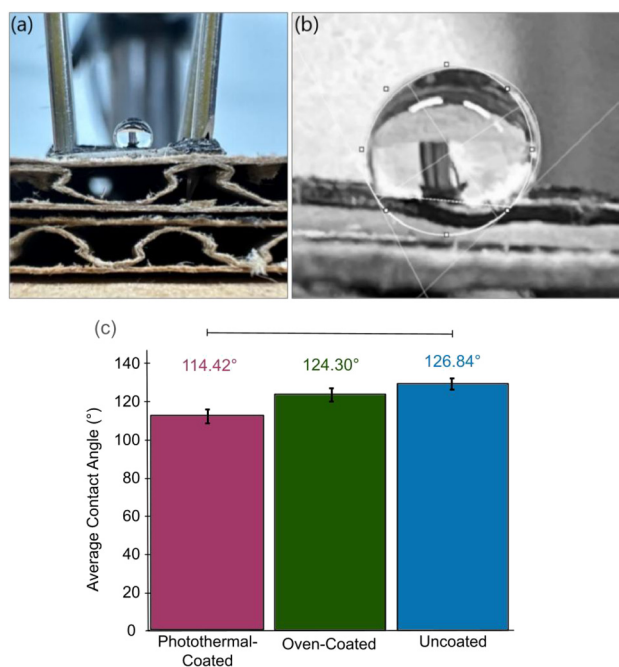
We note that some curvature in the sample is clearly visible within Fig. 5. These long-scale features are known as ‘form’ and is a result of the fact that the substrate is not rigid. We are aware that the presence of this form could alter the measurements of the contact angle. While the sample could have been

adhered to a rigid substrate to force it to be flat for these measurements, deformation of the sample would lead to strain that would change the surface energy and also affect the measured contact angle. Thus, we had to choose between using the sample ‘as is’ and accepting errors due to the presence of form, or choosing to flatten the substrate and accept errors due to changes from introduced strain. We ultimately opted for the former for two reasons. First, the ‘as is’ substrate is a better exemplar of what we directly obtain and, second, the degree of form can be quantified while the added strain due to flattening the sample would not be easily measured. We also note that, across 5 samples, with different forms, we have relatively small error bars, indicating that this measurement is at least consistent across our samples.

The uncoated Stora Enso's paper is marketed as hydrophobic, and so the contact angle observed for the uncoated paper ( $126.84^\circ \pm 2.10^\circ$ ) is not surprising. We found that the contact angles for both PDMS coated samples are lower than for the uncoated sample, though we found that this difference was only significant for the photothermally treated sample ( $p = 0.0141$  according to a Student's *t*-test). Both of the values associated with the PDMS coating also exceed those for bulk PDMS, which has a contact angle range of  $(108^\circ \pm 7^\circ)$ .<sup>28</sup> Usually, the process of coating materials imparts a texture, which has been shown to increase hydrophobicity in PDMS.<sup>33</sup> However, the smaller contact angle for the PDMS coated samples may be due to the fact that the paper is already textured and coated with additional unknown polymers. We were surprised with these results and interpret the lower contact angles to be caused by laser degradation of the PDMS coating on the previously-coated surface, instead of purely uncoated paper. Fig. S11 shows profilometry data obtained for both coated and photothermal-coated conditions that the photothermal-coated samples are, indeed, more rough than the uncoated samples.

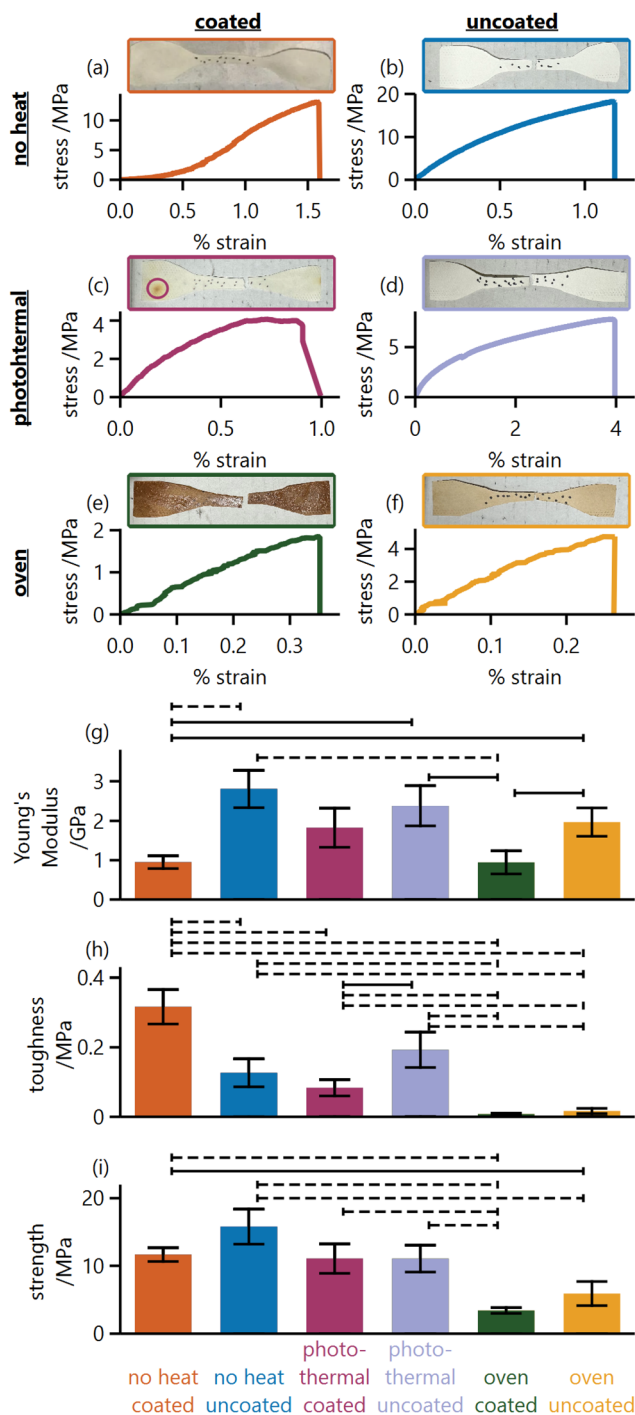
### 3.5. Optical appearance

Fig. 6a–f shows images of tensile sample coupons produced for each of our six conditions, which can also be used to visualize the extent to which the thermal treatments alter the coloration of the paper. Fig. S8 displays these images larger and side-by-side. In these images, it is important to remember that the black marks in the thin neck of the tensile bar are not a result of heating. Instead, they are added by a pen to each sample for tracking of movement during tensile testing (see below). Comparing the appearance to the uncoated paper (Fig. 6b), it is quite clear that the oven-coated sample undergoes the largest change in color, while the sample that undergoes the second largest change is the oven-uncoated sample. From this, we can conclude that the temperature used to drive the oven-curing leads to significant chemical changes to the paper, though we did not attempt to characterize the products of this degradation. We can also see that the unheated-coated paper is a different color from the uncoated paper, likely a result of the different refractive index of PDMS and the inclusion of CB.



**Fig. 5** Results of contact angle measurements. (a) Image of the means by which the paper was held in place with needles. (b) Example of how contact angle is measured. In this image, the contact angle is determined as the average angle between the tangent lines and surface (dotted line). (c) Average contact angles for the photothermal-coated ( $\pm 3.37^\circ$  SE), oven-coated ( $\pm 3.31^\circ$  SE), and uncoated ( $\pm 2.10^\circ$  SE) paper. According to a two-tailed Student's *t*-test, only the photothermal-coated and uncoated samples contact angle measurements that are statistically significantly different at a level of  $p = 0.05$ , and this is indicated by the horizontal line above the bars. Each contact angle assessment photographed for this project can be found in Fig. S5. Contact angles were calculated by fitting an ellipse to the image of the drop and then recording the angle formed between the droplet and the surface.





**Fig. 6** Summary of results from tensile tests. (a–f) Exemplar stress–strain curves obtained from tensile bars of paper produced under our five conditions, as well as images of the bars after fracture (shown above the curves). (g) Average Young's modulus, (h) average toughness, and (i) average strength obtained from 5 measurements. In these plots the error bars indicate the standard error of the average and the horizontal lines indicate those pairs of conditions that are statistically significantly different (solid lines) or very statistically significantly different (dashed lines) using a two-tailed Student's *t*-test for  $p = 0.05$  and  $p = 0.01$ , respectively. For these lines, the lines start and end at the two conditions in the pair.

Turning to the photothermally treated samples (Fig. 6c and d), we note that the photothermal treatment of uncoated paper does alter the color slightly, though substantially less than oven treatment. There is a slightly larger change in appearance for the photothermal-coated paper, however, we again note that the appearance is clearly not as altered as for the oven-coated paper, despite curing occurring on a much faster time-scale. Additionally, the appearance is similar to the unheated coated samples, suggesting that the change in appearance is primarily due to the presence of PDMS and CB. We also note that, though we do not observe large changes in coloration under photothermal heating, this is not because the laser power is insufficient to lead to degradation. We verified this by exposing a spot at the bottom left of the coated sample to 30 seconds of laser irradiation (circled in magenta in Fig. 6c). This exposure clearly leads to a strong discoloration. Thus, the laser light can produce conditions for significant discoloration, but we are able to cure the PDMS film photothermally while minimizing such discoloration.

### 3.6. Tensile testing

To test for differences in mechanical properties of the samples, we performed tensile tests on the tensile coupons shown in Fig. 6a–f. Exemplar stress strain curves for each sample are shown below the corresponding images of the coupons.

The stress–strain curves share a common shape. There is a gradual increase in stress until the paper rips, as seen by the steep drop to zero applied stress on the right side of the graph. When comparing between conditions, it is worth noting that both strain and stress scales change between the plots. Fig. S6 shows all traces plotted on the same scale. In comparing the samples that were heated, the samples heated in an oven break at lower stress and lower strain than those heated photothermally. These results suggest that the mechanical strength of the textiles were reduced by treatment in the oven. Finally, when looking at the unheated-coated sample, we see a breakage at lower stress than the uncoated, comparable stress breakages to the photothermal-coated sample, and higher stress breakages than the oven-coated sample; this suggests that ambiently curing CB-PDMS resembles photothermal conditions.

A more robust comparison of the physical properties are shown in Fig. 6g–i, which shows values for the Young's modulus, toughness, and strength for all conditions, averaged over five samples for each condition. In these charts, the vertical error bars represent standard error of the average, while the solid and dashed horizontal bars connect pairs of conditions that were found to be statistically significantly different ( $p < 0.05$ ) and very significantly different ( $p < 0.01$ ), respectively, using a Student's *t*-test.

In examining these charts, a pattern immediately emerges: the photothermal-coated samples never differ significantly from the uncoated samples. Additionally, the photothermal-coated samples only differ from the unheated-coated samples in terms of toughness. Though the strength of the photothermal coated

sample is lower than the uncoated, we stress that, according to a *t*-test at  $p = 0.05$ , they are not significantly different. We also note that the oven-coated samples' physical properties *always* differ very significantly ( $p < 0.01$ ) from the uncoated sample, and are always reduced relative to the uncoated samples. In other words, treatment in the oven produces a coated textile that is distinctly different, and evidently weaker, than the starting textile, while the photothermal treatment produces a coated textile that preserves the physical properties of the starting textile.

#### 4. Using a lower-temperature oven

In considering the above results, we note two things. First, the same extent of curing is not expected for room temperature cure, and so comparison to the unheated-coated samples may not be the most relevant comparison. Second, the temperature used for the oven-treated samples is quite high, as we were attempting to cure the samples as quickly as possible. Thus, it is also possible that if a lower oven temperature was used, we could cure the polymer to a greater extent while also avoiding the discoloration noted in the section above. To this end, we found that the hottest oven temperature we could use that would not lead to significant discoloration was 85 °C. The manufacturer's recommendation is to cure the PDMS for 105 minutes at this temperature. Fig. S10 shows the results of this treatment, in comparison to all other conditions. We note that the discoloration is not significantly different from the unheated-coated sample, however, both the Young's modulus and toughness is different from the uncoated sample, with the Young's modulus being lower and the toughness being higher. Thus, coating the textile in an oven at this temperature is slower and produces a sample with properties that deviate more from the parent textile than does the photothermal curing.

#### 5. Discussion

The above experiments were designed to compare the degree of curing between photothermal-coated and oven-coated PDMS on a temperature-sensitive substrate, as well as compare their resulting physical properties. Both DSC (Fig. 3) and TGA (Fig. 4) measurements indicate that the PDMS cured photothermally is cured to at least the same extent—if not to a greater extent—than the samples cured using an oven. This result is despite the fact that the heating time for photothermal curing is one-sixtieth (or less) that for oven-curing. The ability of photothermal heating to greatly increase the rate of curing is already known,<sup>14,20–22</sup> and here we show that ability is retained when the thermoset is added as a coating to a temperature sensitive substrate.

Additionally, we also show that this rapid thermal curing does not significantly alter the physical properties of the textile substrate. This is shown in measurements of mechanical properties and color of the textile, where we also see that heating in the oven does significantly alter these properties (Fig. 6). Curing the polymer under ambient conditions for 48 hours or at 85 °C for 105 minutes produces physical pro-

perties that differ from the uncoated paper. We emphasize that these observations are not a value-judgment, as there are times that alteration of the physical properties may be desired. We simply note that photothermal curing provides a means to rapidly cure PDMS on textiles without alteration of the tensile properties.

However, we do note that photothermal curing does provide a difference in the surface properties of the textile, such as contact angle with water droplets (Fig. 5). Specifically, we find that photothermal-coated and oven-coated samples have the same contact angle, which differs significantly from that of the uncoated paper. This demonstrates that, even though the photothermal-coated sample does not alter the tensile properties, it is still able to impart the same surface properties that a conventionally cured polymer does.

In total, we find that when using techniques that probe the *polymer coating* the textile (DSC, TGA, and contact angle), there is little difference between photothermal-coated and oven-coated samples. However, when we consider techniques that report on the properties of the *substrate* (color and mechanical properties) the oven-curing produces significant changes, while the photothermal curing does not (compared to the uncoated sample). Thus, it seems that photothermal heating is able to rapidly drive curing of PDMS on a thermally-sensitive substrate to the same extent that would be done in an oven, at quicker rates, and with less change to the underlying substrate. It should be noted that, though it has been shown that photothermal heating can be used to drive high temperature processes with little change in bulk temperatures,<sup>10,14</sup> our work is a direct test of the idea that this behavior could be used to avoid damaging thermally-sensitive substrates.

Finally, while we note that the data discussed above demonstrates that rapid photothermal curing of PDMS is viable when working with thermally-sensitive materials, the use of a directly commercially-relevant substrate (Stora Enso coffee cup paper) does lead to some caveats. For instance, we do not know the exact composition of the textile, or what the chemical nature of the surface prior to coating is. It is possible that the nature of this substrate somehow imparts a unique thermal stability to photothermal heating and further tests on other substrates are warranted. We highlight, though, that manufacturers, such as Stora Enso, already coat textiles and have a desire for this type of process, so further characterization of the paper was not conducted. In addition, we have not attempted to identify the chemical nature of the changes to the paper after heating. Thus, we are unsure if the changes seen for the oven-coated samples are a result of combustion, pyrolysis, or some other chemical transformation. However, it remains clear that thermal treatment can change the nature of the textile, and that photothermal heating can, to a large extent, avoid such changes. Moreover, we have demonstrated this is the case directly for a thermally-sensitive substrate that is commercially relevant. We believe that these results could be realized for other thermally-sensitive substrates, such as other textiles, electronics, and even living tissue.



## 6. Conclusions

We have demonstrated that photothermally heating PDMS on paper can cure the polymer to the same extent as a more traditional oven-heating approach, but in a fraction of the time. The polymers produced have similar properties at their interface, as measured by contact angle of water, but the two heating approaches have different effects on the underlying paper substrate, as measured by color and mechanical properties. While curing in an oven results in significant changes to both, photothermal heating largely leaves these properties undisturbed. This work demonstrates that photothermal heating can be used to drive high-temperature chemical reactions on top of thermally-sensitive substrates, achieving the desired chemical transformation and leaving the substrate largely unchanged.

## Author contributions

All authors contributed to the conceptualization of the experiments, data analysis, data visualization, and the writing and editing of the manuscript. APB and APK additionally conducted data acquisition and BJL was responsible for funding acquisition and project administration.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Data for this article, including all data used to make the figures, are available in the Pennsylvania State University Archives at <https://doi.org/10.26208/A8EK-DV49>.

Supplementary information: DSC of pure PDMS, photos comparing uncoated, and PDMS coated paper (with and without CB), photos of tensile instrument. See DOI: <https://doi.org/10.1039/d5lp00130g>.

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