The chemical, mechanical, and physical properties of 3D printed materials composed of TiO$_2$-ABS nanocomposites

Matthew R. Skorski$^a$, Jake M. Esenther$^a$, Zeeshan Ahmed$^a$, Abigail E. Miller$^{a,c}$ and Matthew R. Hartings$^a$

$^a$Department of Chemistry, American University, 4400 Massachusetts Ave., NW, Washington, DC, 20016, USA
$^b$Thermodynamic Metrology Group, Sensor Science Division, Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
$^c$Food and Drug Administration, Washington, DC, USA

ABSTRACT
To expand the chemical capabilities of 3D printed structures generated from commercial thermoplastic printers, we have produced and printed polymer filaments that contain inorganic nanoparticles. TiO$_2$ was dispersed into acrylonitrile butadiene styrene (ABS) and extruded into filaments with 1.75 mm diameters. We produced filaments with TiO$_2$ compositions of 1, 5, and 10% (kg/kg) and printed structures using a commercial 3D printer. Our experiments suggest that ABS undergoes minor degradation in the presence of TiO$_2$ during the different processing steps. The measured mechanical properties (strain and Young's modulus) for all of the composites are similar to those of structures printed from the pure polymer. TiO$_2$ incorporation at 1% negatively affects the stress at breaking point and the flexural stress. Structures produced from the 5 and 10% nanocomposites display a higher breaking point stress than those printed from the pure polymer. TiO$_2$ within the printed matrix was able to quench the intrinsic fluorescence of the polymer. TiO$_2$ was also able to photocatalyze the degradation of a rhodamine 6G in solution. These experiments display chemical reactivity in nanocomposites that are printed using commercial 3D printers, and we expect that our methodology will help to inform others who seek to incorporate catalytic nanoparticles in 3D printed structures.

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1. Introduction
Additive manufacturing, or three-dimensional printing, encompasses a number of techniques in which a material is deposited in a layer-by-layer fashion to produce a larger 3D structure.[1, 2] A diversity of materials (sugars,[3] thermoplastics, photopolymers,[4] glass,[5] metals,[6] metal oxides,[7] and ceramics,[8] to name a few) are used to produce 3D printed figures. Of these, thermoplastics are the most common for home enthusiasts and experimental laboratories due to the large number of commercially available printers that employ these materials, which results from the safety, ease of use, and cost of the equipment. Thermoplastics are extruded at temperatures above their glass transition temperature ($T_g$), at which they display increased flexibility and flow properties.

Commercial thermoplastic 3D printers have found their way into several research laboratories. Despite their popularity, their use has been mostly confined to producing tools that assist in performing research rather than producing structures that are subjects of research. This is especially true for the chemical sciences. Taken from a chemist's point of view, a printed item is primarily an inert object.

That is not to say that chemists and (bio)materials scientists have not found innovative ways to use 3D printing to advance their fields. Cronin and co-workers...
have developed 3D printed reactionware using acetoxy silicone polymers that are normally used as household sealants.[9–11] Their reactionware has been used to facilitate syntheses, purifications, crystallizations, and analyses. Another subject where 3D printing has great potential is in the area of tissue engineering. Several groups of scientists have printed hydrogels that have been seeded with mammalian cells.[12–14] The hydrogels are fixed into place with UV light, and the cells are allowed to culture within the printed scaffold. In each of these examples, a polymer with optimal flow properties at room temperature is extruded and induced to set through some external stimulus (light, oxygen, etc.).

While 3D printing holds great promise for advancing chemistry and materials science, this promise has not been realized for the ubiquitous thermoplastic printers. We contend that one way to imbue active chemistry into 3D printed thermoplastic objects is to incorporate inorganic nanoparticles into the polymer filaments. Because organic dye molecules are infused into a polymeric matrix to create different colored filaments, inorganic nanoparticles should be able to be integrated in much the same way. The functionalities associated with different types of nanoparticles (catalysis,[15] luminescence,[15] thermal,[16] and electric,[17] conductivity, and gas storage,[18] to name a few) should retain their properties when incorporated into a thermoplastic. We have incorporated TiO₂ nanoparticles into acrylonitrile butadiene styrene (ABS) filaments. The TiO₂-ABS filaments were printed in multiple shapes and tested for their mechanical, physical, and chemical properties. TiO₂-polymer nanocomposites have been studied in detail.[19–24]

Nanocomposites are materials in which nanoscale particles have been incorporated into a polymer matrix. In many nanocomposites, advantageous properties of the nanoparticles and the polymer are maintained in the bulk material. In some nanocomposites, enhancement of functional properties is observed. TiO₂ has been shown to increase the mechanical strength of the nanocomposite over the pure polymer.[20, 22, 24] TiO₂ can increase the dielectric properties of a polymer for use in insulating materials.[21] TiO₂ nanocomposites can also photocatalytically degrade environmental organic pollutants.[24] 3D printed TiO₂-ABS nanocomposites should follow similar trends, and 3D printing of this material could become a viable way to fabricate custom, on-demand parts that can meet any number of these technological needs. In the experiments presented here, we aim to determine if printed TiO₂-ABS composites maintain the advantageous properties of the nanocomposites as described above.

TiO₂ nanoparticles make an ideal test case for an inorganic nanoparticle filler within thermoplastic printing filaments. TiO₂ is a known photocatalyst, capable of generating free radical species in both aqueous and organic solvents and in the presence of oxygen upon irradiation.[25] The band gap of TiO₂ corresponds to UV wavelengths. Upon absorbance of light, electrons in the conduction band can form superoxide radicals (O₂•⁻) from adsorbed oxygen, and holes in the valence band can form hydroxyl radicals (∗OH) from water. Because of these properties, TiO₂ has potential applications in the photocatalytic removal of pollution from air, water, and agricultural sources.[26, 27] It also has potential uses in solar energy [28] and solar hydrogen production.[29] The use of TiO₂ nanoparticles in many consumer products, such as paints, means that this material is abundant and can be acquired at low cost. All of these factors – low cost, ease of purchase, and readily testable chemical properties – make TiO₂ an ideal test case for producing functional nanocomposite ABS filaments.

We present here detailed observations of several chemical, physical, and mechanical properties of 3D printed TiO₂-ABS nanocomposites. We describe the preparation and evaluation of a range of TiO₂-ABS compositions (0, 1, 5, and 10% kg/kg). There is one previous study of the mechanical properties of printed 5% TiO₂-ABS structures.[22] Our measurements generally agree with the previous observations and expand upon the analysis of how TiO₂ affects the properties of printed ABS. As there are few studies of 3D printed TiO₂-polymer nanocomposites, we have attempted to understand how the different processing steps affect the chemical and physical properties of the polymer. We determined the effect of TiO₂ on the thermal transitions and the molecular weight of the processed (solvent cast, extruded, and printed) ABS. We measured the ability of the TiO₂ to quench the luminescence that arises from the styrene functional groups within ABS. Finally, we analyzed the photocatalytic degradation of rhodamine 6G by 3D printed structures of TiO₂-ABS nanocomposites. We expect that these experiments will inform future studies in which nanoparticles are incorporated into thermoplastic 3D printing filaments for developing chemically active 3D printed materials.

2. Materials and methods

2.1. Materials

Titanium(IV) oxide (nanopowder, 21 nm particle size by transmission electron microscopy, 80–90% anatase polyform with small percentage of rutile polyform) and rhodamine 6G were purchased from Sigma Aldrich (St Louis, Missouri, USA).[30] Commercial ABS filament was purchased from Octave Systems (Santa Clara, California, USA) (natural color, 1.75 mm width). High Performance Liquid Chromatography (HPLC)-grade water, dimethylformamide (DMF), and acetone were purchased from BDH Chemicals (Radnor, Pennsylvania, USA). ABS pellets (resin: GPA 100; color #: NC010; color: natural; lot #: C14–0702 K) was acquired from LTL Color Compounders, Inc. LiBr was purchased from Acros Chemicals (New Jersey, USA).
2.2. Production and printing of TiO$_2$-ABS filaments

ABS and TiO$_2$ mixtures (0, 1, 5, and 10% TiO$_2$ by dry weight) were suspended and dispersed in acetone (in a sealed container) over several hours at 35°C in a sonicator (VWR Symphony ultrasonic cleaner, VWR, Inc., Radnor, Pennsylvania, USA). The highest percentage of TiO$_2$ used in this study was 10% (kg/kg) because we found that nanocomposites produced at higher percentages were incompatible with our printing process. A typical batch included 20 total grams of ABS and TiO$_2$ in 200 ml of acetone. As an example, a 1% sample was made by suspending 0.2 g of TiO$_2$ and 19.8 g of ABS in 200 ml of acetone, held in an Erlenmeyer flask, and agitated in a heated sonicating bath. The dispersed samples were solvent cast in Teflon coated, aluminum holders. DSC was performed using a TA DSC Q2000 from TA Instruments (New Castle, Delaware, USA). Roughly 3 mg of nanocomposite sample was placed in an aluminum Tzero pan (TA Instruments) and sealed with a hermetic lid (TA Instruments). Samples were exposed to the following heating cycle. The temperature was increased from 20 to 170°C at a rate of 10°C min$^{-1}$, held at 170°C for 2 min, decreased from 170 to 20°C at 10°C min$^{-1}$ and held at 20°C for 2 min. These cycles were repeated for a total of three full heating and cooling cycles.

Polymer sizes were measured using a Straygrel HR 4 THF GPC column (7.8 mm × 300 mm, Milford, Massachusetts, USA) attached to a Waters 1525 HPLC system (Standards SM-105 from Shodex, Tokyo, Japan). Polymer molecular weights were calibrated with polystyrene standards (Shodex Standards SM-105). Samples were prepared for GPC by dissolving the polymer in 0.05 M LiBr in DMF and filtering through a 0.45 μm-pore syringe filter.

2.4. Effect of TiO$_2$ and processing on ABS structure

To determine if processing (solvent casting, extruding, and printing) ABS in the presence of TiO$_2$ affects the polymer structure, we measured monomer content with Fourier transform infrared spectroscopy (FTIR), ABS thermal transitions with differential scanning calorimetry (DSC), and polymer size with gel permeation chromatography (GPC). FTIR spectra were recorded using a Bruker Alpha spectrometer (Billerica, Massachusetts, USA) with an attenuated total reflectance solid sample holder. DSC was performed using a TA DSC Q2000 from TA Instruments (New Castle, Delaware, USA).

2.5. Fluorescence data

All fluorescence measurements were recorded using a Perkin Elmer LS-55 luminescence spectrometer from Perkin Elmer (Watham, Massachusetts, USA). The ability of TiO$_2$ to quench the natural fluorescence of the styrene within the printed polymer was tested. Cylinders (2.5 cm diameter, 50 cm height) were printed with no raft. The side of the cylinder that was in contact with the print bed during fabrication was the smoother of the two sides. These procedures do not result in a cylinder that is flat enough for fluorescence measurements. A single drop of acetone was placed on the top of the cylinder and the window from the sample holder was set on top of the drop for 30 min before fluorescence measurements to flatten the cylinder. Performing this step increased the reproducibility of the data. Multiple cylinders were printed for each per cent TiO$_2$ in ABS, and each cylinder was measured six times. The cylinder was rotated within the sample holder in between each measurement. Emission spectra were collected with an excitation wavelength of 280 nm with a slit width of 10 nm and the emission slit width was set to 4.5 nm. Emission was scanned from 300 nm to 550 nm. The scan speed was 200 nm min$^{-1}$. The emission spectra were corrected such that the emission goes to zero at 550 nm.
The total integrated emission intensity was calculated for each measurement.

To test the photocatalytic properties of TiO$_2$ in the printed nanocomposites, we placed one half of a printed dogbone in a scintillation vial and immersed it in 10 ml of a 1 μM aqueous rhodamine 6G solution. The fluorescence of the solution was recorded before and after the sample was exposed to direct sunlight for 4 h. To measure fluorescence, the solution was placed in a quartz cuvette. Emission spectra were collected with a 480 nm excitation with a 10 nm slit width and an emission slit width of 10 nm. The emission was scanned from 500 nm to 650 nm. The total integrated intensity was calculated for each spectrum to determine if the TiO$_2$ in the printed materials could photocatalytically degrade the rhodamine 6G. As photogenerated radicals might also affect the ABS polymer, we recorded the FTIR spectra of printed dogbones before and after 4 h of exposure to direct sunlight.

3. Results and discussion

While developing our system we performed a number of preliminary experiments and observations. First we had to choose the polymer for making nanocomposites. The two polymers that are typically used in consumer 3D printers are ABS and polylactic acid (PLA). We chose to work with ABS as opposed to PLA for this work because we observed that PLA is more prone to decomposition during extrusion (experimental observation). One observation that we made while printing the TiO$_2$-ABS composites is that the standard printing speed (30 mm s$^{-1}$) led to poorly printed structures and often led to clogged print heads. We found piano wire to be the best tool for cleaning these clogs. Reducing the printing speed to 10 mm s$^{-1}$ resulted in consistent, quality structures. We also would like to note the importance of allowing the print heads and printing bed to remain at operating temperature for at least a half an hour before starting a print job. This increased the temperature inside of the printing chamber and reduced the chances that the structure would curl up from the print bed during the print job.

3.1. TiO$_2$ in ABS

Figure 1 shows the XRD patterns of TiO$_2$. 0% TiO$_2$ in ABS (1%), 1% TiO$_2$ in ABS (1%), 5% TiO$_2$ in ABS (5%), and 10% TiO$_2$ in ABS (10%). The 1, 5, and 10% samples show the presence of TiO$_2$. The intense peak (at 2θ = 25.4°) from the anatase polymorph of TiO$_2$ is present in all TiO$_2$-ABS samples along with the signal (at 2θ = 27.5°) from the rutile polymorph of TiO$_2$. The signal of all TiO$_2$-associated peaks increases (with respect to the broad ABS signal at 2θ = 20°) with increasing percentage of TiO$_2$ within the ABS composite. Full spectra (from 2θ = 3° to 2θ = 90° are shown in the Supporting Information).

3.2. Effect of TiO$_2$ and processing on ABS structure

ABS is formed when styrene and acrylonitrile are polymerized in the presence of pre-formed polybutadiene creating a network of polybutadiene and poly(styrene-co-acrylonitril) polymers. The solvent casting, extrusion, and printing steps place a significant amount of strain on the ABS. The presence of TiO$_2$ during these processes can exacerbate any damage to the polymer. Because TiO$_2$ can photocatalytically produce free radicals,[25] ABS can be degraded and altered throughout the progression from solvent casting to printed structure. To understand how each preparation step affected the polymeric structure, we monitored the FTIR spectra, glass transition temperature, and polymer molecular weight at different points in the processing for all of the TiO$_2$-ABS nanocomposites used.

FTIR analysis assesses how the individual components (acrylonitrile, butadiene, and styrene) are affected during the processing steps. Figure 2 displays the FTIR spectra for 3D printed samples (dogbones and cylinders). Multiple spectra were recorded for each TiO$_2$ percentage. The averaged spectra are shown in the top panel while the bottom panels show the average transmittance with standard deviations for the wavelengths associated with different components of the ABS-TiO$_2$ nanocomposite.

The data corresponding to TiO$_2$ absorption (absorbance feature at 465 cm$^{-1}$) show increasing amounts of TiO$_2$ with increasing TiO$_2$ percentage within the nanocomposite. These data are in agreement with the data in Figure 1. The spectra in Figure 2 are taken for printed samples, therefore the data show that TiO$_2$ remains...
nanoparticles do not contact the polymer matrix. If TiO$_2$ is capable of facilitating polymer degradation, samples with less clumping will increase degradation. We contend that TiO$_2$ dispersity in the 1% sample leads to increased polymer–nanoparticle interactions. The increased number of nanoparticle-polymer interactions in the 1% sample lead to changes in absorption features and, potentially, increased polymer degradation during processing. Increased deviations observed for the acrylonitrile, butadiene, and styrene FTIR peaks are due to increased polymer–nanoparticle interactions. This description (increased clumping leading to fewer interactions between the polymer and the nanoparticle) is consistent with other experimental observations, which will be discussed below.

ABS is naturally amorphous and displays no melting or crystallization features. ABS has a glass transition temperature ($T_g$) at roughly 105°C. The $T_g$ values of the different nanocomposites are shown in Figure 3. The $T_g$ of an unprocessed ABS pellet (unaltered from the supplier) and of the lab-extruded 0% TiO$_2$ ABS filament are both near the published value of 105°C. The

The data for acrylonitrile ($\lambda_{\text{abs}} = 2237$ cm$^{-1}$), butadiene ($\lambda_{\text{abs}} = 910$ cm$^{-1}$), and styrene ($\lambda_{\text{abs}} = 698$ cm$^{-1}$) paint a different picture. None of these absorption features differ significantly from the samples printed with commercial ABS filament and lab-extruded (0% TiO$_2$) ABS filament. There are no trends observed in these samples with increasing TiO$_2$ concentration. This result is to be expected, as the sample matrices are still primarily ABS.

The standard deviations for the acrylonitrile, butadiene, and styrene features associated with the 1% TiO$_2$ samples are markedly higher than those of the other samples. The deviation in the 1% samples (±1.7, 9.2, and 16.9% for acrylonitrile, butadiene and styrene, respectively) is clearly larger than the deviation observed for the 5% and 10% TiO$_2$ samples. We argue that, as the amount of TiO$_2$ is increased in the nanocomposite, the amount of nanoparticle clumping increases. As the clumping increases, the direct net interactions between ABS and TiO$_2$ decreases. That is, because some TiO$_2$ nanoparticles are sequestered within aggregates, these nanoparticles do not contact the polymer matrix. If TiO$_2$ is capable of facilitating polymer degradation, samples with less clumping will increase degradation. We contend that TiO$_2$ dispersity in the 1% sample leads to increased polymer–nanoparticle interactions. The increased number of nanoparticle-polymer interactions in the 1% sample lead to changes in absorption features and, potentially, increased polymer degradation during processing. Increased deviations observed for the acrylonitrile, butadiene, and styrene FTIR peaks are due to increased polymer–nanoparticle interactions. This description (increased clumping leading to fewer interactions between the polymer and the nanoparticle) is consistent with other experimental observations, which will be discussed below.

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Figure 2. FTIR spectra for printed TiO$_2$-ABS composites. The top panel includes the full spectrum for each composite, averaged over 10 printed samples. The bottom panel displays the % transmittance at wavelengths associated with the different components for the TiO$_2$-ABS composites. The error bars correspond to the standard deviation from the averaged measurement over all spectra acquired. In these spectra, different colors (for the lines in the upper panel and circles in the bottom panels) correspond to samples printed from different composites. Gray: commercial ABS filament. Red: extruded 0% TiO$_2$-ABS composites. Green: extruded 1% TiO$_2$-ABS composites. Blue: extruded 5% TiO$_2$-ABS composites. Purple: extruded 10% TiO$_2$-ABS composites.
weight data were determined with the calibration curve (described above) using the Bluez software that controls the Waters HPLC system. Several samples for each processing step were acquired. The PDI, which is calculated by dividing the molecular weight average ($M_w$) by the number average molecular weight ($M_n$), is indicative of the molecular weight distribution of the polymers in solution. $M_w$ decreases from the value observed for the ABS pellet for each ABS–TiO$_2$ sample except for the solvent cast 10% TiO$_2$ sample. We argue that the mass difference between the polymer from the ABS pellet and the solvent cast 10% TiO$_2$ sample are statistically insignificant; a variation of 10 kDa is within the expected error of the measurement for the column used here. The change in molecular weight is largest for the 1% sample. This observation is consistent with the result showing that greater dispersion of TiO$_2$ in the 1% sample leads to more ABS decomposition (Figure 2). From the data in this table, it would appear that most of the polymer degradation occurs during the solvent casting process. In this step, ABS is sonicated with TiO$_2$ at 37°C in acetone, poured into a Teflon coated pan, and heated at 80°C to evaporate the solvent. The effects of the other processing steps on polymer size seem to be less than the effect of the casting step. To support these data, we have also measured the FTIR spectra of the nanocomposites after each processing step. These spectra are presented in the Supporting Information.

### 3.3. Mechanical properties of the printed TiO$_2$-ABS nanocomposites

TiO$_2$ has previously been shown to alter the mechanical properties in printed ABS.[22] This type of observation is consistent with other experiments on TiO$_2$-polymer nanocomposite materials.[20, 23] As opposed to other nanocomposite structures, 3D printed structures have natural striations resulting from the printing resolution. It is possible that the printing process affects the homogeneity of the nanocomposite. We measured the mechanical properties of the printed materials to test the effect of these qualities and to directly study the effect of TiO$_2$ on ABS. ASTM D638 standard dogbones were printed and analyzed using a Series 5 Universal Testing Machine from Mark-10 (Copiague, New York, USA) for stress-strain and three-point bending measurements.

Figure 4 shows the stress-strain curves measured for 5% TiO$_2$-ABS dogbones, and Figure 5 shows the flexural testing results of these same materials. Several mechanical properties calculated from these experiments are shown in Table 1.

| TiO$_2$ Concentration | $M_w$ (kDa) | PDI |
|-----------------------|------------|-----|
| 1%                    | 170 (1.9)  |     |
| 5%                    | 180 (1.8)  |     |
| 10%                   | 220 (1.7)  |     |

Table 1. Molecular weight and polydispersity index (PDI) determination for ABS after each processing step.

The predominant cause for decreased $T_g$ in the ABS that contains TiO$_2$ is the nanoparticle–polymer interaction. It has been observed that TiO$_2$ reduces the glass transition temperatures in polymeric systems where there is poor interfacial adhesion, leading to an increase in free volume and polymer chain mobility near the particle.[32–34] The $T_g$ data are consistent with the FTIR spectra. Increasing the dispersion of the nanoparticles within the polymer matrix will increase the total surface area of TiO$_2$ available to ABS. If the 5% and 10% samples contained dispersed nanoparticles, the $T_g$ values would decrease for these nanocomposites consistent with the amount of TiO$_2$ added. We contend that the $T_g$ for the 5% and 10% samples do not decrease in comparison to the 1% sample due to nanoparticle aggregation.

The molecular weight of the ABS at different stages of processing was analyzed using GPC. Polystyrene standards were used to correlate retention time to molecular weight. The data for these standards were fit using a quadratic equation (shown in the Supplemental Information) to determine the molecular weight of the processed polymer. Table 1 shows the peak molecular weight ($M_w$) and polydispersity index (PDI) data for the TiO$_2$-ABS nanocomposites after: solvent casting, extruding through the compounder, extruding into a 1.75 mm filament, and 3D printing.

The retention time was determined by selecting the peak maximum in the recorded GPC trace. Molecular

The change in molecular weight is largest for the 1% sample. This observation is consistent with the result showing that greater dispersion of TiO$_2$ in the 1% sample leads to more ABS decomposition (Figure 2). From the data in this table, it would appear that most of the polymer degradation occurs during the solvent casting process. In this step, ABS is sonicated with TiO$_2$ at 37°C in acetone, poured into a Teflon coated pan, and heated at 80°C to evaporate the solvent. The effects of the other processing steps on polymer size seem to be less than the effect of the casting step. To support these data, we have also measured the FTIR spectra of the nanocomposites after each processing step. These spectra are presented in the Supporting Information.

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tensile and flexural measurements, therefore the interaction between the polymer and the nanoparticles (21 nm) must have an adverse effect on the strength of the material matrix. As the nanoparticles clump together, there are several possible mechanisms that might lead to an increase in material strength. The first of these possibilities is that the effective size of the TiO$_2$ plays a role in determining tensile and flexural strength. As the effective particle gets larger (and the surface area to volume decreases), the total number of particle–polymer interactions decrease. If the interaction itself has an adverse effect on the strength of the matrix, decreasing the number of interactions will increase the strength. This possibility is consistent with the increased polymer flexibility near the nanoparticles that leads to a decrease in $T_g$.\[33\] Another possibility is that individual polymer chains can intercalate between nanoparticles within a single clump. The intercalation might make the polymer matrix stronger. We expect that the strength (justified by either of the two descriptions) will eventually stop increasing as a function of particle clumping, which has also been shown to induce fracture points in nanocomposites with high loading percentages.\[20\] We should note that in the previous study on 3D printed TiO$_2$-ABS structures, the researchers only prepared a 5% TiO$_2$ nanocomposite.\[22\] They observe an increase in tensile strength over the 0% nanocomposite. This observation is consistent with our experiments.

### 3.4. Photocatalytic degradation of rhodamine

TiO$_2$ and TiO$_2$ nanocomposites have been shown to generate reactive oxygen-based radicals when exposed to sunlight.\[25\] These radicals can take part in reactions with organic compounds in close proximity to

### Table 2. Mechanical properties and measurement uncertainties for average stress, average strain, Young’s modulus, and flexural strength of each nanocomposite.

| Mechanical testing | Average stress (MPa) | Average strain (%) | Young’s modulus (MPa) | Flexural strength (MPa) |
|--------------------|---------------------|--------------------|-----------------------|------------------------|
| 0% TiO$_2$         | 41.4 ± 0.7          | 9.0 ± 0.2          | 6.1 ± 0.2             | 70 ± 2                 |
| 1% TiO$_2$         | 39.4 ± 0.8          | 8.9 ± 0.3          | 6.1 ± 0.5             | 62 ± 5                 |
| 5% TiO$_2$         | 43.6 ± 0.2          | 9.7 ± 0.8          | 6.2 ± 0.7             | 72 ± 8                 |
| 10% TiO$_2$        | 43 ± 1              | 9.1 ± 0.9          | 6.5 ± 0.4             | 72 ± 2                 |
surrounds the TiO$_2$ can also be degraded by the photo-generated radicals, we measured the FTIR spectra before and after a 6 h solar exposure. Over this time period, we observe some minimal degradation of the ABS polymer (data shown in the Supporting Information). Because of the promising results described above, we have begun to experiment with different printed geometries to determine an optimal printed shape for applications that involve photocatalytic removal of environmental pollutants.

4. Conclusions

We have developed a process for generating TiO$_2$-ABS nanocomposite filaments for application in 3D printing. We have reported on the physical, mechanical, and chemical properties of these materials after they have been printed. The analysis of rhodamine 6G degradation characterizes the chemical and catalytic activity of a material that was produced using a commercial thermoplastic 3D printer. We expect to expand upon these studies by incorporating other, chemically active nanoparticles within ABS and bring new chemistry to 3D printed materials.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

At the time of publishing, Skorski and Esenther are both undergraduates at American University. Ahmed is on staff at the National Institutes of Standards and Technology whose primary research focus is on materials for photonics sensing. Miller has recently moved from a faculty position at American University to the United States Food and Drug Administration. Hartings is a faculty member at American University who studies a broad range of polymer-transition metal nanoparticle nanocomposites, which includes areas that vary from biomineralization to synthesizing the types of industrial polymer nanoparticle systems described in this manuscript.

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