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Temperature-insensitive silicone composites as ballistic witness materials: the impact of water content on the thermophysical properties

Ran Tao^{1,2,*} , Fan Zhang¹, Huong Giang Nguyen¹, Philip Bernstein³, Amanda L. Forster¹, Randy A. Mrozek⁴, and Aaron M. Forster^{1,*}

¹ Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

²Department of Chemical Engineering, Texas Tech University, Lubbock, TX 70409, USA

³Department of Mechanical Engineering, Frostburg State University, Frostburg, MD 21532, USA

⁴CCDC ARL, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA

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ABSTRACT

In this work, different formulations of a room-temperature silicone composite backing material (SCBM) composed of polydimethylsiloxane (PDMS), fumed silica and corn starch were investigated using different characterization techniques, i.e., differential scanning calorimetry, thermogravimetry analysis, X-ray diffraction (XRD) and small-angle X-ray scattering, as a function of controlled relative humidity. At ambient relative humidities in the range of about 20–80%, the equilibrium water content in the SCBM ranges from approximately 4–10%, which is predominantly absorbed by the corn starch. This amount of water content has been shown to have minimal effect on thermal transition temperatures (melting and glass transition) of the SCBMs. The enthalpy of melting increases with increasing relative humidity, which reflects the heterogeneous semicrystalline structure of starch granules and the role of moisture in facilitating the formation of amylopectin double helices mainly in the imperfect crystalline regions. The thermal degradation of SCBM exhibits three major mass loss steps that correspond to dehydration, decomposition of corn starch and decomposition of PDMS. The XRD patterns reveal a characteristic diffuse peak for amorphous PDMS and an A-type crystallinity for the corn starch. The XRD results

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Address correspondence to E-mail: ran.tao@nist.gov; aaron.forster@nist.gov

show no observable changes in the crystal type and crystallinity as a function of moisture content. Results from this work help clarify the fundamental structure– property relationships in SCBMs, which are important for future development of documentary standards, especially the handling and storage specifications of next-generation ballistic witness materials for body armor testing.

GRAPHICAL ABSTRACT



Introduction

A backing material, or ballistic witness material (BWM), is required for a complete ballistic evaluation of body armor [1–3]. Armor must be designed not only to defeat a ballistic threat, but also to reduce the transfer of energy to the wearer to levels less than that which may cause life-threatening injuries from blunt trauma [4]. Current law enforcement standards require that the behind-the-armor indentation depth when a projectile does not perforate the armor, also known as the backface deformation, does not exceed 44 mm [4]. The BWM serves as the recording medium during armor testing, from which the backface deformation is measured. The BWM is required to exhibit a constant depth of deformation when subjected to impact by a projectile of a known geometry, velocity and input energy. Prior to using the BWM in ballistic testing, its performance is validated by a drop test in which an impactor with specified mass and geometry indents a ballistic clay known as Roma Plastilina No. 1 (RP1) [5], and the depth of indention determines the usability of the RP1 [6]. A prominent concern for the current standard BWM is temperature dependent properties that introduce undesired variation into ballistic resistance tests. Furthermore, its formulation has not remained consistent over time [7, 8]. When RP1 was originally formulated in the

1970s for use as a modeling clay, it was also used at room temperature for ballistic testing. However, as the manufacturer has changed the formulations to address the needs for the modeling community, the ballistic-use temperature has had to increase over the years in order to continue to meet BWM validation standards. The ballistic-use temperature in 2012 was approximately 40 °C [9]. The search for an alternative BWM with minimal temperature dependence to replace the current clay began in 2010 [10]. Recently, a synthetic room-temperature silicone composite backing material (SCBM), developed by the US Army Research Laboratory, emerged as a promising candidate BWM [11–14]. Unlike RP1, which is formulated from a non-specified number of natural materials, the SCBM consists of three components, and these are non-cross-linked linear polydimethylsiloxane (PDMS), fumed silica and corn starch. The SCBM formulation exhibits similar quasi-static mechanical properties, drop validation and ballistic testing results at room temperature as RP1 when it is used at its currently specified ballistic-use temperature (40 °C) [11]. Using the SCBM at room temperature is a significant improvement to using the RP1 at 40 °C [11–14]. Prior to implementation of the SCBM into armor testing methodologies, a comprehensive material properties study is required to fully understand this new material.

Our previous work [14] has addressed measurement challenges in quantifying the effects of strain, strain rate and temperature on the mechanical properties of the SCBMs using shear rheology. Meanwhile, our rheological results indicate that the SCBMs become stiffer after aging at ambient conditions and exhibit stiffness reductions after handworking in a way analogous to the mechanical working process applied to the BWM during its preparation for armor testing. The BWM is worked to fit into a rectangular-prism-shaped test box for ballistic testing. The storage modulus for the aged SCBM increases by approximately 25% as compared to the as-received material, and the storage modulus for the handworked SCBM is about 10% lower than that of the as-received material [14]. Although the changes in the stiffness magnitude do not appear to affect the overall SCBM response to ballistic impact [11], it is important to understand the structural and physical behavior effects as a function of storage conditions. Two factors that may contribute to the structural changes within the SCBM were considered [14]: (1) the hygroscopic ingredient, namely the corn starch, may absorb water and cause changes in the physical and structural state [15]; and (2) filler network reorganization of the fumed silica particles may also alter the stiffness over time [16]. Since those materials are generally stored in a ballistic range at ambient conditions and are reusable upon repackaging into the test box, it is beneficial to evaluate the material properties in a controlled manner, particularly when subjected to different humidity conditions.

In this work, we provide detailed compositional information on the SCBM formulation as a promising backing material for ballistic testing. Furthermore, we use а combination of thermophysical and microstructural characterization tools to investigate the SCBM as a function of exposure to controlled relative humidity conditions. Native corn starch granules are semicrystalline materials composed of highly branched amylopectin and primarily linear amylose molecules [17, 18], and their thermophysical properties can be drastically affected by the presence of water [19, 20]. We first evaluate the water content in the SCBMs with different compositions in various humid environments and then measure the phase transition and decomposition temperatures, as well as molecular structure of the SCBMs by thermal analysis and X-ray diffraction. Finally, we perform small-angle X-ray scattering measurements to

estimate the size of the aggregated silica in the composites. This is the first study on the investigation of thermophysical properties of the SCBM as a function of controlled relative humidity. The drying and conditioning procedure is similar to the heat-moisture treatment for the corn starch [21], a common hydrothermal treatment method used in starch processing. The results gained in this work also provide valuable information for the use of corn starches for non-food applications.

Experimental

Materials

The SCBM materials were prepared by the Army Research Laboratory (Aberdeen Proving Ground, MD, USA) from starting materials of non-crosslinked, trimethylsiloxy-terminated DMS-T41 PDMS with a molecular weight of 62,700 g/mol (Gelest, Inc., Morrisville, PA [5]), CAB-O-SIL M7D untreated fumed silica (Cabot Corp., Boston, MA) and Argo corn starch with a granule size of $15 \pm 10 \ \mu m$ (ACH Food Company Inc., Memphis, TN). The amylose-toamylopectin ratio by weight in Argo corn starch has reported to be between 28.7 and 71.3 previously [22]. Three formulations of SCBM, designated as SCBM #1, SCBM #2 and SCBM #3, were investigated. The formulation details of the SCBMs are provided in Table 1. In order to focus on the role of corn starch on the interaction with moisture, a batch of SCBM #2 was generated without the corn starch component (denoted as starch-free SCBM #2), but the PDMS-tofumed silica volume ratio was kept similar to the SCBM #2 formulation. The approximate densities for the PDMS, corn starch and fumed silica used for volume to mass conversion are 0.97, 1.5 and 2.1 g/ cm³, respectively. The detailed preparation procedure and processing conditions have been previously reported [11]. Briefly, the three components were premixed using a commercial countertop stand mixer until the mixture was visually homogeneous. The mixture was further loaded into a ram feeder attached to a 16 mm twin screw extruder (PolyLab OS/ PTW16, ThermoFisher Scientific, Waltham, MA [5]) with a 40 L/D barrel at a feeding rate of 4.2 kg/h and screw speed of 100 rpm.

Prior to the humidity exposure, all materials were pressed into a flat layer of approximately 2 mm to **Table 1** Formulation detailsof the SCBMs investigated^a

Materials	Fumed silica (mass %)	PDMS (mass %)	Corn starch (mass %)	
SCBM #1	6.2	39.4	54.4	
SCBM #2	6.8	39.0	54.2	
SCBM #3	7.2	38.7	54.1	
starch-free SCBM #2	14.9	85.1	0	

^aThe standard uncertainty of mass fraction is \pm 0.5 (mass %)

increase surface area, placed on a glass petri dish, then placed into a forced air oven with desiccant and dried at about 130 °C for approximately 3 h. The materials were cooled to room temperature within the oven at the temperature set point of about 25 °C for approximately 1 h. The drying procedure has similarities to a heat-moisture treatment, where the starch is heated above the gelatinization temperature but at moisture levels below that required for gelatinization [21]. This process has been shown to dehydrate the amylose crystals and amylopectin double-helical structure in the amorphous region and alter crystal polymorphs in certain types of starch granules, while causing no observable changes on the crystalline structures for others [23, 24]. Nevertheless, such treatment is not expected to alter the size or shape of the starch granules [21, 23, 24]. After drying, the materials were immediately placed into temperature and humidity conditioning chambers at three relative humidity (RH) levels, i.e., 27, 40 and 80% RH, denoted as RH 27, RH 40 and RH 80, all at 25 °C for approximately 720 h. This conditioning step is also referred to as "aging" of the SCBMs in the Results section. The environmental chambers used provided control to ± 1 °C and $\pm 5\%$ RH [25]. The temperature and humidity were closely monitored using temperature and humidity data loggers over the course of the exposure of the materials in the environmental chamber.

Moisture sorption isotherm

The moisture sorption studies were performed gravimetrically using a VTI-SA⁺ automated vapor sorption analyzer (TA Instruments, New Castle, DE [5]) at ambient pressure and approximately 25 °C. Approximately 8.5 mg (wet mass) material was used for each measurement. The specimens were initially dried in situ at about 140 °C for 4 h under a flow of pure nitrogen and then equilibrated at around 25 °C for 3 min prior to starting the water sorption

isotherm measurement process. The dynamic vapor sorption system controls the RH set point by continuously mixing a dry nitrogen flow with a humid nitrogen flow. The RH steps were increased from 10 to 90% RH at 10% RH increment intervals. The maximum equilibration time for each step was set to 3500 min, which allows for a steady-state data acquisition (within 0.001 mass % change over 99 min) at all RH levels. The mass resolution is \pm 0.1 µg and the standard uncertainty for humidity control is \pm 1% RH based on the manufacturer specifications for the vapor sorption analyzer.

Thermal analysis

Calorimetric measurements were taken under a nitrogen atmosphere using a TA Q2000 differential scanning calorimeter (TA Instruments, New Castle, DE). The mass of the DSC specimens ranged from about 5 mg to 10 mg. The specimens were sealed in 40 µL hermetic aluminum pans for measurement by heating from about 25-400 °C at a heating rate of nominally 10 °C/min. Measurements were taken in triplicate. The DSC temperature calibration was performed using the melting point (T_m) of three different standard materials: indium ($T_m = 156.6$ °C), tin (T_m -= 231.9 °C) and lead (T_m = 327.5 °C). The heat flow calibration was performed using indium (ΔH_{m-1} = 28.6 J/g). For all measurements, the melting temperature was determined as the onset of the first endothermic melting peak, and its enthalpy change (ΔH_m) was calculated from the area under the peak using a linear baseline.

The thermal decomposition behavior of the SCBMs was measured using a TA Q500 thermogravimetric analyzer (TGA) under dry air flow. The mass of TGA specimens, placed in 100 μ L platinum pans for measurement, ranged from about 6 mg to 12 mg. At least three runs were performed on each sample to verify reproducibility. The specimens were heated from approximately 30–130 °C at a heating rate of

nominally 10 °C/min, followed by a 30 min isotherm at approximately 130 °C to allow dehydration. Heating was then continued to about 800 °C at a heating rate of nominally 10 °C/min. The decomposition temperatures are reported as the extrapolated onset temperature of degradation T_{onset} (defined as the intersection of the starting-mass baseline and the tangent line through the point of the maximum gradient during the mass loss), T_{peak1} (the first peak temperature of the time derivative of the mass loss curve, d(mass)/dt) and T_{peak2} (the second peak temperature of the d(mass)/dt curve).

X-ray diffraction and small-angle X-ray scattering

X-ray diffraction (XRD) measurements were taken using a Bruker D8 Advance diffractometer (Bruker AXS, Inc., Billerica, MA) equipped with an EIGER2 R 500 K (Dectris, Inc., Philadelphia, PA) single-photoncounting detector. The monochromatic X-ray wavelength was 1.5418 Å from Cu K α radiation. The XRD scans were focused on a 2 θ range from about 10°–30°, where prominent XRD peaks reflecting molecular order are present. XRD data were acquired in the Bragg–Brentano geometry. The specimens were placed on a Si-based zero-diffraction plate with specimen thicknesses \approx 1 mm. Data reduction was conducted using Bruker DIFFRAC.EVA version 5.0 software.

An extensive length scale structural characterization was performed on a subset of the specimens using the ultra-small-angle X-ray scattering (USAXS) instrument at the Advanced Photon Source, Argonne National Laboratory [26]. The combined scattering and diffraction measurements probe the microstructure and molecular order in a continuous size range from sub-angstrom to several micrometers. Measurements were taken in a transmission geometry, in contrast to the reflection geometry of the laboratorybased XRD measurements. The X-ray energy was nominally 21 keV, corresponding to an X-ray wavelength of about 0.5904 Å, ensuring complete transmission of the nominally 1-mm-thick specimens. More details about the instrument setup can be found elsewhere [27]. The measurements were also taken on a mechanically worked SCBM #2 specimen which was kneaded by hand for about five minutes. The same handworking process was used in our previous work [14].

Results and discussion

Moisture sorption results of the three SCBMs investigated are shown in Fig. 1, where the water content is plotted as a function of RH measured at 25 °C gravimetrically; also shown are data for the starchfree SCBM #2. The adsorption isotherms for the three SCBMs are sigmoidal in shape and statistically similar (within 95% of the confidence interval), which is as expected because the three formulations only differ in their PDMS-to-fumed silica ratio. The Guggenheim-Anderson-de Boer (GAB) equation was used to model the water sorption data, which adequately describes the equilibrium water content in the SCBM formulations at 25 °C, as shown by the solid lines in Fig. 1. The values of the GAB parameters are listed in Table S1 in Supplementary Information. These values are comparable with the values found for the GAB model applied to corn starch powder measured at 30 °C [28]. From our results, at a laboratory ambient condition of 50% RH, an equilibrium water content of approximately 7% for the SCBM is anticipated. When equilibrated at nominal ambient humidities of 20-80% RH, the SCBMs are expected to contain about 4% to about 10% moisture. In contrast, the sorption data for the starch-free SCBM #2 specimen exhibit minimal water uptake



Figure 1 Moisture sorption isotherms of SCBM #1, SCBM #2, SCBM #3 and the starch-free SCBM #2 specimen at steady-state conditions measured at different RH levels and 25 °C. The solid lines are fits to the GAB model. The dashed lines are the 95% confidence interval bounds for the mean value of the water content data from different formulations. The GAB fitting parameters are reported in Table S1.



over the RH levels studied, as shown by the purple hexagons in Fig. 1, indicating that the corn starch is a dominant contributor to the moisture adsorption in the SCBMs. Since the mass fraction of the corn starch is approximately 54% in the SCBM (Table 1), assuming the water is held solely in the corn starch granules, we estimate that the equilibrium water content in the corn starch granules to range between 7.4% to 18.5% at the investigated ambient humidities. This result is in a good agreement with previously reported steady-state water content of amorphous corn starch ranging from 7 to 21% at 25 °C and in RH conditions ranging from 20 to 80%, respectively [15, 20]. According to Schmidt et al. [29], the water content for Argo corn starch is 8.7% at a_w of 0.287, again consistent with our results-within the 95% confidence interval range for the water content at a RH of 28.7%, which ranges from 8.5 to 9.6% on a corn starch mass basis (Fig. 1).

Thermal analysis was utilized to investigate phase transition and decomposition temperatures for the SCBMs. Differential scanning calorimetry (DSC) detects the heat flow changes associated with both first- and second-order transition phenomena of materials, such as crystallization, melting and glass transition. Figure 2 shows the normalized DSC heat flow responses for SCBM #2 aged at different humidity conditions. The primary feature detected in the aged thermograms is an endothermic peak at around 140 °C observed for the SCBMs at the nominal 27, 40 and 80% RH conditions. This peak is attributed to the melting of corn starch crystals, specifically, the amylopectin double helices [20, 30]. Note that this endothermic peak is absent for the dry material, as shown by the black curve, meaning no melting transition is observed. The DSC thermogram for the dry SCBM is similar to those obtained when SCBMs were stored at ambient temperature and humidity, and then dried in situ using a DSC pan with a pin-hole lid to allow release of moisture, as previously reported [13]. The loss of the melting peak in the dry SCBM material is a result of the drying protocol where water is driven out of the specimen and the molecular order is diminished or lost. When the specimens are exposed to humid conditions, containing around 4-10% moisture (RH 27-RH 80), the semicrystalline amylopectin is able to re-establish some degree of molecular order and crystallinity facilitated by the absorbed water. A second endothermic peak with a maximum is detected in the



Figure 2 DSC heating scans at nominally 10 °C/min for SCBM #2 at different RH levels and the starch-free SCBM #2. The bottom left downward arrow represents the endothermic direction. The heat flow curves are offset for clarity of presentation. Thermal parameters are given in Table 2.

range of 260–300 °C, which is related to breakage of long macromolecular chains in the corn starch [31, 32], leading to a full thermal degradation of all of its molecules, as shown by the subsequent large decomposition exotherm in the temperature range of about 300–330 °C [33]. The starch-free SCBM does not exhibit either the melting peak around 140 °C or the degradation signal, see the purple curve in Fig. 2.

Based on measurements of multiple specimens of a given SCBM, the melting temperature (T_m) and enthalpy of melting (ΔH) are plotted in Figure S1 for all of the SCBMs investigated, and the values are tabulated in Table 2. The melting temperatures at different humidity conditions are statistically similar with the highest standard deviation being 13% of the mean value. Meanwhile, the enthalpy of melting shows an increasing trend with increasing RH for all three SCBMs. It is also noted that the shape of the melting peak varies across different specimens. Figure 3 shows representative results of the heat flow responses for different SCBMs at a RH of 80%, where the melting transition for the three materials exhibit a broad peak, a sharp peak and a split peak, as indicated by the solid, dashed and dotted lines, respectively. This variability is reflected in the standard deviation of the peak area, or ΔH_m , within 8% for each material at a specific RH level, with broader peaks resulting in a slightly lower T_m (Table 2). The magnitude of the DSC enthalpy of melting have been

Materials		T _m (°C)	ΔH (J g ⁻¹)	T _{onset} (°C)	T_{peak}^{1} (°C)	T_{peak}^2 (°C)	T_{peak}^{3} (°C)	Residue at 800 °C (%)
SCBM #1	RH 27 RH 40	145.4 ± 3.9	91.7 ± 7.0 111.5 + 8.9	292.0 ± 1.1	305.6 ± 1.4	380.6 ± 6.2	494.6 ± 20	13.6 ± 0.6
	RH 80		163.8 ± 9.1					
SCBM #2	RH 27	142.7 ± 5.8	102.8 ± 2.9	291.5 ± 1.6	305.6 ± 1.2	385.6 ± 3.2	510.9 ± 16.8	14.8 ± 0.6
	RH 40		121.1 ± 1.4					
	RH 80		171.7 ± 13.5					
SCBM #3	RH 27	148.9 ± 9.5	92.3 ± 6.5	291.1 ± 0.6	305.3 ± 1.1	384.2 ± 2.5	509.9 ± 10.7	16.7 ± 1.6
	RH 40		106.0 ± 8.1					
	RH 80		172.8 ± 12.2					

Table 2 Thermal properties of the SCBMs investigated for this work^a

 ${}^{a}T_{m}$, melting temperature; ΔH_{m} , enthalpy of melting; T_{onset} , the onset temperature of decomposition after the isothermal holding step; T_{peak} , peak temperatures in the d(mass)/dt curves as indicated in Fig. 4. The uncertainties are standard deviation of the mean (n > 3)

reported to correspond with a reduction in the double-helical molecular order, rather than loss of crystallinity in starches [34]. The variation in temperature range and sharpness of the melting peaks indicate that amylopectin, a highly branched component that forms a double-helix structure in native starch [35] and contributes to crystallinity, exists in various degrees of double-helical order in the aged SCBMs. This can be understood by the complex, heterogeneous semicrystalline structure of starch granules. Specifically, the crystalline regions are predominantly contributed by short chains of amylopectin that



Figure 3 DSC heating scans at 10 °C/min for different SCBM formulations conditioned at a RH of 80% in the entire measurement temperature range. The heat flow curves are offset for clarity of presentation.

closely pack into double helices, while the long amylopectin chains pass from the crystalline region into the amorphous regions which contain both nonordered, linear amylose and branching points of amylopectin [15, 36, 37]. Amylose is also considered to intersperse among amylopectin molecules, thus existing in both the crystalline and amorphous regions [36, 38]. Previous studies have shown that the amylopectin in the heterogeneous amorphous (or imperfect crystalline) regions may contain a significant amount of double-helical components that are not involved in extended, regular crystalline arrays. Therefore, the level of double-helical molecular order in starch is much greater than crystalline order [17, 34]. The observed increasing trend in ΔH with RH but with no obvious change in T_m may suggest that moisture facilitates amylopectin chains organizing into an ordered (double-helical) form but does not necessarily alter the crystallinity or crystal size.

The phase behavior and thermal properties of corn starch have been reported to depend on water content and starch composition, i.e., amylose-to-amylopectin ratio and lipid contents [20, 30, 39, 40]. Most previous work has been focused on the gelatinization of corn starch and thus has examined only high hydration levels as compared to those found in the SCBMs. At these high hydration levels, multiple endotherms (i.e., gelatinization endotherm, melting of amylose–lipid complexes, etc.) have been observed. In contrast, in the present study, only one endothermic melting peak is detected before degradation. Another transition phenomenon that may be



Figure 4 TGA curves measured at 10 °C/min for SCBM #2 at different RH levels. Inset figure shows the rate of the mass loss as a function of temperature (DTG curve). See Table 2 for degradation temperatures.

detected by DSC for a semicrystalline material is the glass transition, where the amorphous regions of the material transform from a glassy state into a rubbery state. Water content is shown to have significant effect on corn starch T_{g} . In particular, at moisture levels above 20%, T_g drops below room temperature [15, 19, 20, 30]. This T_g depression could have implications for thermal processing and storage of starch products [19] because it influences molecular mobility and, therefore, changes the kinetics of starch gelatinization and retrogradation [18, 37]. However, from our results, the amount of water content in corn starch shows no effect on the glass transition of the SCBMs. Therefore, we infer that T_g from corn starch does not have a significant impact on SCBM properties at ambient storage conditions. Detailed discussion is provided in Supplementary Information.

Thermogravimetry is used to evaluate thermal stability and decomposition for SCBMs. The TGA curves of the SCBM #2 conditioned at different RH are shown in Fig. 4. The inset figure shows the first derivative of the mass loss with respect to time, d(mass)/dt, as a function of temperature. The deriva-(DTG) tive thermogravimetric curves are characterized by three minima, at which the peak temperatures are denoted as T_{peak}^{1} , $T_{\text{peak}}^{2}^{2}$ and T_{peak}^{3} . The values of the decomposition temperatures and residue at 800 °C are reported in Table 2. There are three major mass loss steps in the overall

decomposition process. The first step is related to dehydration that starts immediately from ambient temperature to 130 °C. A subsequent isothermal step holding at this temperature for 30 min ensures complete dehydration [31]. As shown in Fig. 4, materials with higher moisture content exhibit greater mass loss until the completion of the isothermal step, as expected. The approximate total mass losses at the end of this step are 4.7, 5.9 and 7.5% for the RH 27, RH 40 and RH 80 specimens, respectively, which are close to the equilibrium water content values at those RH levels measured in the present study, i.e., 4.8, 6.0 and 10.2% (Fig. 1). As temperature increases, the second mass loss step starts with the onset temperature (T_{onset}) of around 290 °C. The peak temperature of around 306 °C (T_{peak}^{1}) in the DTG curve (Fig. 4 inset) is a characteristic pattern for corn starch, which is related to a complete breakdown of polyhydroxy groups in starch accompanied by depolymerization [32, 33, 41]. The initial moisture content does not affect the decomposition temperatures because the water has already evaporated [32], as dehydration and decomposition are generally considered as two separate processes for the degradation mechanisms of corn starch [32, 33]. The initial breakdown of corn starch is endothermic [32, 42], as seen in the DSC heating scan at temperatures starting at approximately 260 °C (Fig. 2) and replotted in Figure S3 with the TGA curve for comparison. As decomposition progresses, the endotherm turns into an exothermic process that is associated with gaseous combustion [42]. The final mass loss step for SCBM degradation is from around 370-530 °C, which corresponds to the degradation of PDMS. This process comprises two decomposition stages, namely thermo-oxidation and thermal depolymerization [43-45], as revealed by the second and third peaks in the DTG curves. The oxidative process around 380 °C (T_{peak}^2) involves silicon-methyl group oxidation and cross-link formation [43], and the third peak (T_{peak}^3) is thermal depolymerization of the siloxane backbone into cyclic oligomers [45]. A 6% variation in T_{peak}^2 and a 20% variation in T_{peak}^{3} locations are observed for different specimens from multiple measurements (Fig. 4 inset and Table 2), which may be attributed to the uncertainty in the removal of the volatile oxidation and decomposition products from the heterogeneous sample product system with the purge gas at high temperatures [45]. The TGA results for the other two SCBM formulations are similar, and the only difference is the amount of residue at 800 °C. As shown in Table 2, the residue increases from SCBM #1 to SCBM #3, which is consistent with the increase in silica content for those materials.

X-ray diffraction is a technique commonly used for the assessment of crystal structure in a crystalline or a semicrystalline material. The X-ray diffraction patterns for the SCBM #2 specimens conditioned at various RH levels are presented in Fig. 5; also shown are the data for the starch-free SCBM # 2 specimen. For a semicrystalline material, distinct peaks diffracted by the ordered crystalline structures are expected to superimpose on an amorphous background. For all materials examined, a broad diffuse peak at around 11.7° is observed, which corresponds to the amorphous structure of PDMS [46]. Individual peaks are observed in the diffractograms for SCBMs containing corn starch at around 15° and 23°, with a doublet observed around 17° and 18° (2 θ). These reflections are characteristic peaks for a typical Atype polymorph for the amylopectin crystals [47, 48]. The A-type pattern has been previously reported for native corn starch with low or medium amylose contents [19, 47-49]. A minor peak is observed at around 20° (2 θ), which is indicative of a V-type crystallinity [47, 49]. The V-type diffraction pattern is also characterized by two other main reflections at around 7° and 13° (2 θ) [50]. Although the V-type pattern is rarely observed except for high-amylose corn starch [17], it provides evidence for the presence of amylose-lipid complexes. The amylopectin double



Figure 5 X-ray diffraction patterns for SCBM #2 at different RH levels and the starch-free SCBM #2. The intensity curves are offset for clarity of presentation.

helices exist in crystalline regions that are closely packed into regular arrays [17, 34], as well as in amorphous phases along with the single helical amylose, located between crystallites, which contributes to the amorphous background. Therefore, a proper decomposition of crystalline (sharp) and amorphous (diffuse) intensity profiles is required in order to estimate the degree of crystallinity from the XRD patterns [51]. Such imperfection of the corn starch crystal structures can be recognized by the broad diffraction peaks in Fig. 5. Lopez-Rubio et al. [51] have described a peak fitting procedure for the calculation of starch crystallinity using a crystal defect approach, which also allows for separating contributions from different crystal polymorphs. Our XRD data were obtained for a multicomponent and multiphase system, which makes the definition of the amorphous background even more difficult. Thus, the crystallinity is not quantified in the present study. Overall, the XRD patterns for the four SCBMs containing corn starch are qualitatively similar. Different moisture content does not induce significant changes to the A-type crystal peak locations, consistent with previous findings for corn starch [19]. There is seemingly an increase in the peak intensities as RH increases from 27 to 40%. Previous studies have reported either an increase [49] (from 10 to 30% moisture level) or a decrease [52] (from 18 to 27% moisture level) in the intensity of the X-ray diffraction for corn starch upon hydration. Those effects may be attributed to the differences in the starch composition and heat-moisture treatment conditions (time and temperature) used, which resulted in different changes in the arrangements of the crystalline regions [21]. The starch-free SCBM displays amorphous diffractogram patterns (the purple curve in Fig. 5), as expected, since all characteristic peaks are attributed to the diffraction of the corn starch crystals. The dry corn starch, shown by the black curve, exhibits a small degree of crystallinity despite the lack of the melting endotherm in the DSC measurement. This may be attributed to the differences in the time interval between specimen preparation and experiment, i.e., the XRD measurement was taken after transferring the specimen to a different laboratory location which introduces additional delay between measurements. Although the material was properly sealed, trace amounts of moisture can easily diffuse into a hygroscopic dry material. As a result, the diffractogram for the dry material is similar to



that of the RH 27 material with a water content of 4.6% (Fig. 1).

In order to discern the effect of water content and structure rearrangement of the fumed silica network structure, additional SAXS and USAXS measurements are taken for a handworked SCBM #2 specimen (conditioned at RH 40). The handworking process is expected to disrupt any transient structures [8, 14]. In practical use, the BWM is effectively worked on a regular basis during the course of body armor evaluation. The SAXS data are summarized in Fig. 6. The scattering data suggest three observed structure levels indicated by the dashed lines that highlight three power-law slopes. Specifically, the first structure level (P1), between 0.03 and 0.2 \AA^{-1} , is related to the primary particles; the second level (P2), between 0.002 and 0.02 $Å^{-1}$, represents aggregates of the primary particles; and the third level (P3), below



Figure 6 A log-log plot of the reduced, slit-smeared scattering intensity vs. the magnitude of the scattering vector q for the SCBM #1, SCBM #2, SCBM #3 and handworked SCBM #2 (all conditioned at RH 40). The dashed power-law slopes indicate three scattering levels, with P1, P2 and P3 corresponding to primary particles, aggregates and agglomerates, respectively.

 0.002 Å^{-1} , refers to agglomerates of silica aggregates. This behavior is typical for polymer composites where structure heterogeneity persists across many length scales and strongly correlates with the material's properties and surface energy [53]. Using this hierarchical structure as a basis, we performed a Unified analysis [54] on the SAXS data. Detailed information is provided in Supplementary Information.

The primary particle and aggregate sizes are shown in Table 3. Unsurprisingly, the primary particle size is material-independent, which supports the model validity. In addition, the primary particle size acquired from this SAXS analysis is consistent with previous TEM observation from freeze-fracture sample of the same type (M7D) fumed silica [55]. The aggregate size, on the other hand, depends on the material formulation and condition. For the unworked materials, interestingly, the aggregate sizes of the three formulations decrease slightly, although not statistically significant, with increasing silica-to-PDMS volume ratio. This may be explained by the bridging between the hydroxyl group on the silica surface and the oxygen atoms of the PDMS backbone [56, 57], that is, with more PDMS chains available, stronger interfacial interactions between fumed silica and PDMS take place, which promotes dispersion quality. It may also be indicative of the sensitivity of the aggregate size to the fumed silica concentration and processing conditions. The increase in fumed silica content leads to more aggressive mixing conditions during processing (blending and extrusion), which leads to more breakup of the dominant aggregate size. The handworked specimen contains aggregates with a nominal size 20% greater than its unworked counterpart. This suggests that the applied macroscopic strains during handworking break down loose agglomerates of fumed silica that are connected by adhesion forces, facilitating a microscopic rearrangement in the form

Table 3 Primary particle size and aggregate size extracted	Materials	Primary particle size (nm)	Aggregate size (nm)
from SAXS analysis for the SCBMs investigated ^{<i>a</i>}	SCBM #1	24.8 ± 1.6	155.4 ± 10.0
	SCBM #2	24.0 ± 2.0	147.8 ± 10.2
	SCBM #3	24.4 ± 1.6	141.2 ± 9.2
	SCBM #2 (worked)	24.6 ± 1.8	178.6 ± 13.8

^aThe materials are all conditioned at RH 40. The uncertainties are standard errors from model fitting

of larger aggregates, resulting in the softening of the material [14].

Conclusions

In this work, we investigated different formulations of a room-temperature silicone composite backing material (SCBM) composed of PDMS, fumed silica and corn starch, which is designed to be used as a ballistic witness material in standardized body armor testing. Moisture sorption measurements, differential scanning calorimetry, thermogravimetry analysis, X-ray diffraction and ultra-small-angle X-ray scattering techniques were employed to study the structure–property relationships in SCBM as a function of controlled RH. Detailed formulation information for the SCBM was provided and this correlates well with the results obtained. Major findings include:

- 1. At ambient RH of 20–80%, the equilibrium water content in the SCBM ranges from 4 to 10%. The moisture is adsorbed predominantly by the corn starch, as supported by the moisture sorption results on a starch-free SCBM specimen, as well as the agreement between the estimated equilibrium water content on a corn starch basis and the values reported for pure corn starch in the literature.
- 2. The amount of water content shows no effect on thermal transition temperatures (with melting around 145 °C and glass transition temperature of around 58 °C) of the SCBMs, or that these changes are below the detection limit. Particularly, the increasing trend observed in the enthalpy of melting with increasing RH can be understood by the heterogeneous semicrystalline structure of starch granules, which suggests that moisture facilitates the formation of amylopectin double helices mainly in the imperfect crystalline regions.
- The degradation of SCBM measured from ambient temperature to 800 °C exhibits three major mass loss steps, which correspond to dehydration, decomposition of corn starch and finally decomposition of PDMS.
- 4. The XRD patterns reveal the diffuse peak for amorphous PDMS and an *A*-type crystallinity for the corn starch. The XRD results show no

observable changes in the crystal type and crystallinity as a function of relative humidity.

5. Through SAXS analysis, we infer that the breakdown of agglomerates in the SCBM by the handworking process may help silica aggregates rearrange into larger sizes. However, this aspect of the analysis may deserve further investigation with in situ SAXS during shear for full confirmation.

To summarize, corn starch is the only hygroscopic ingredient in SCBM and the SCBM is stable across a wide range of atmospheric conditions with minimal effect of the water content on its thermophysical properties. The information gained in this work helps in understanding the fundamental structure–property relationships in the candidate ballistic witness material SCBM developed by the US Army, which is important for the acceptance of SCBM by ballistic researchers and the standards-based body armor testing community for future development of documentary standards, especially the handling and storage specifications related to next-generation BWMs for body armor testing.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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