Investigation of commercial cut-resistant gloves claiming graphene additive content

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Abstract. Five commercially available cut-resistant gloves were sourced from four different world-wide manufacturers which were advertised to contain graphene. A method was developed to assess the fibers composing each glove, including dissolution of the constituent fibers using sulfuric acid or liquid paraffin at elevated temperature in order to extract and analyze particle additives.

Scanning electron microscopy with energy-dispersive x-ray spectroscopy was applied to fibers and extracted particles for morphological and elemental analysis, while Raman spectroscopy was applied to discern the composition of carbonaceous materials for the ultimate purpose of identifying any graphenic additives.

Only one of the five tested products contained conclusive evidence of material in the graphene family, as graphene oxide was clearly presented as advertised.

Two of the products, which were sourced from the same manufacturer, contained signatures most indicative of graphite rather than graphene. The remaining two products exhibited signatures of amorphous carbon without evidence of graphitic or graphenic material.

The four products that did not conclusively present evidence of advertised graphene also contained prolific alternative cut-resistant additives such as steel wire, glass fiber, or a silicon-based particle surmised to be silicon carbide. Methods and techniques for the evaluation of products claiming graphene content are demonstrated for the purposes of improving market integrity and consumer confidence in product claims.

1.   Introduction

Since its remarkable properties were conclusively isolated and demonstrated in 2004[1], graphene has found a broad range of theoretical and practical applications from exotic electronics to commodity composites[2]. The meteoric rise in popularity has yielded opportunities for positive product association; items that 'contain graphene' garner increased attention and attraction to the purchasing public regardless of whether its inclusion actually imparts a desirable enhancement.

Markets that gain association with popular additives are susceptible to false claims, which may include omission of the claimed ingredient or substitution of a related and more readily available surrogate. In some cases, these alterations are intentional while others are innocent; product manufacturers may use feedstocks purchased in good faith that do not in fact contain the claimed ingredient, or a lack of expertise may result in erroneous attribution or identification. Regardless of intentionality, consumer confidence (and even safety) depends upon the verification and validation of claimed ingredients.

A range of third party certification labels exist for food products, with definitions honed through the practice of scientific exploration as well as legal settlement[3]. Various consumer products also face scrutiny of claimed ingredients[4], including agricultural products[5]. Reported contamination in commodity products are reported[6, 7], but studies and programs demonstrating the validity of claims of specific additives, especially engineered nanomaterials, are generally less prolific.

Graphene has been identified as a candidate for increasing the strength-to-weight ratio of polymer composites[8-11] and has therefore found commercial use in a wide variety of benefiting applications from kayaks[12] to tennis racquets[13]. As products increasingly contain (or claim to contain) graphene, it is important for the safety of consumers and for the integrity of the market that these claims are met with metrics and methods for validation. To this point, a recent study[14] assessed 34 distinct powders or suspensions, 32 of which were advertised as graphene oxide with the remaining two marketed under a different moniker, judging only 4 to satisfy the advertised label when subjected to rigorous investigation.

As a case study, we investigated five commercially sourced cut-resistant glove products from four distinct brands that advertised inclusion of graphene. These gloves were sourced among popular brands from manufactures in the United States, Europe, and Asian/Pacific regions and assessed using the same developed protocol. Only one product was determined to contain conclusive evidence of content from the graphene family (in the form of graphene oxide). Two products from the same brand appeared to contain graphite particles, while the remaining two products did not exhibit any evidence of graphenic or graphitic material under the applied sampling and characterization conditions.

The protocol developed and described below may find use in a wider variety of products that claim to contain graphene-polymer composites. Through application of these extraction and characterization techniques, regulators, customers, and trade representatives can validate quality and identify misattribution of composition and properties.

2.   Materials and Methods

The five tested glove products claiming graphene content were acquired on the open market; brand names and descriptions are anonymized as Glove A-E. Glove A and Glove B were different product lines from the same brand, while Glove C, Glove D, and Glove E represented individual products from distinct brands.

Characterization was performed on segments of the glove material as received as well as after acid or solvent extraction in order to separate particle additives from the polymer fiber matrix. Material swatches were sampled from regions at the back of the hand and fingertip in order to assess the base fibers as well as the rubberized coating, where present.

A   **B**   **C**   **D**   **E**

Particle extractions were performed using sulfuric acid (ACS Reagent Grade 95.0-98.0%, Sigma-Aldrich), liquid paraffin (Lamplight Ultra-Pure, Ace Hardware), or decahydronaphthalene (cis + trans reagent grade, 98%, Sigma-Aldrich). Sulfuric acid extractions were performed at room temperature, mixing swatches in acid without dilution via magnetic stir bar overnight. In most cases, a portion of the fibrous material would dissolve in sulfuric acid (likely nylon or related composition). Any remaining fabric material was then removed and rinsed with deionized water before solvent extraction, while particles were extracted from the acid and dissolved material using a luer-lock syringe attached to a 13mm polypropylene Swinnex filter holder with a polypropylene filter of nominal 5.0 μm pore size (Sterlitech). The acid solution was then forced through the filter, followed by rinsing with deionized water.

Glove E completely dissolved in sulfuric acid, requiring no additional steps for extraction. An additional fiber variety remained after the sulfuric acid processing of Gloves A-D; Gloves A-B also contained a steel wire mesh that did not dissolve in sulfuric acid or solvent. Extraction of remaining polymeric fibers from Gloves A-D (estimated to likely be composed of a form of high molecular weight polyethylene) was performed via solvent at elevated temperature.

Solvent extractions were performed by addition of the fibrous swatches remaining after sulfuric acid extraction to separate vials containing either decahydronaphthalene (also known as decalin) or liquid paraffin. These vials were heated to 170°C in a sand bath and mixed with magnetic stir bars for 7 hours. While dissolution of remaining material was successfully achieved using both solvents, dissolution occurred more rapidly and completely in liquid paraffin; these samples were selected for subsequent processing and characterization.

Solvent-extracted particles were filtered immediately upon removal from heat using glass fiber prefilters (Merck Millipore) and a Buchner funnel with vacuum. After extraction (by both acid and solvent methods) filters were cut, with one portion used to perform direct analysis by scanning electron microscopy (SEM). For SEM, filters containing the extracted particles were mounted to 12.7 mm aluminum stubs using conductive carbon tape (Ted Pella). A second portion of each filter was placed in a vial with ethanol (95% denatured, lab grade, Aldon Corporation) and stirred vigorously via stir bar overnight to release filtered particles. The mixture was then pipetted onto a hot silicon wafer (Ted Pella) and dried; silicon substrates provide a relatively clean background for subsequent Raman spectroscopy, whereas the filter materials would have exhibited prominent interfering peaks and/or deformed under the laser.

Scanning electron microscopy was performed in a FEI Quanta 600 FEG Environmental SEM equipped with energy dispersive x-ray spectroscopy (EDS, Bruker). Prior to analysis, samples were

coated with an 8 nm-thick conductive platinum-palladium coating using a Leica ACE600 sputter coater.

Raman spectroscopy was performed using a WITec Alpha 500 confocal Raman spectroscope equipped with a 100x and 10x objective lens. A 532 nm laser (<1mW at sample) and grating of 1800 grooves/mm were used for mapping. Raman spectra were collected through the 100x objective with 0.5 μm step size and integration time of 0.2s over the scanned area, where relevant.

Raman spectroscopy is recognized as a required technique for the identification and discernment of different phases of carbonaceous nanomaterials like graphene[15-17]. Direct Raman assessment of glove/fiber surfaces was not expected to be definitive since penetration depth would be limited and signal from any embedded graphene may not be reliably detected. Any comparison between gloves composed of differing materials may therefore be impaired.

Penetration depth varies by material; at a laser wavelength of 532 nm, metals such as silicon may only allow penetration at less than submicron depths[18], while depths up to hundreds of micrometers have been reported in biological tissue (albeit generally with some augmentation to the Raman instrumentation)[19]. Many polymers reportedly allow penetration depths of a few micrometers or even tens of micrometers[20] which might be considered to be just deep enough to render confusing results since glove fibers in this study were generally measured at tens to hundreds of micrometers in diameter. Dissolution of the glove fibers and capture of remaining particulates was therefore determined to be the most reliable technique for assessing all glove samples with objective equivalence.

3. Results

3.1. SEM-EDS Analysis

SEM-EDS was conducted on as-received glove fibers to observe general morphology and discern any elemental signatures of interest. Subsequently, fibers were digested via acid and solvent and remaining particles were filtered and analyzed using the methods described above before conducting similar SEM-EDS analyses.

Several interesting features were noted during SEM-EDS assessment of as-received glove fibers. Glove A and Glove B, which were sourced from the same manufacturer, presented similarly; representative images obtained during analysis of Glove B are presented in Figure 1. Under backscatter detection it was possible to discern inclusions of higher atomic number (z-contrast) embedded within the glove fibers; EDS indicated these particles were silicon-based. Oxygen signatures did not appear to overlay consistently with these particles and no other elements of interest appeared within limits of detection; it is therefore deduced that the particles were likely composed of silicon carbide (as opposed to silicon dioxide). Metallic wire was also observed to be woven throughout the polymeric fibers of Glove A and Glove B samples. EDS analysis detected significant iron and chromium signatures, suggesting the composition to be a variety of stainless steel.

No obvious graphenic morphologies were observed after dissolution and filtration of the Glove A and Glove B fibers. In Figure 2, flake-like particles measuring several micrometers thick were occasionally observed after complete dissolution of fibers by both acid and solvent extraction, most closely resembling graphite flakes. After acid extraction (but before solvent extraction of remaining fibers), silicon-based particles were prevalent.
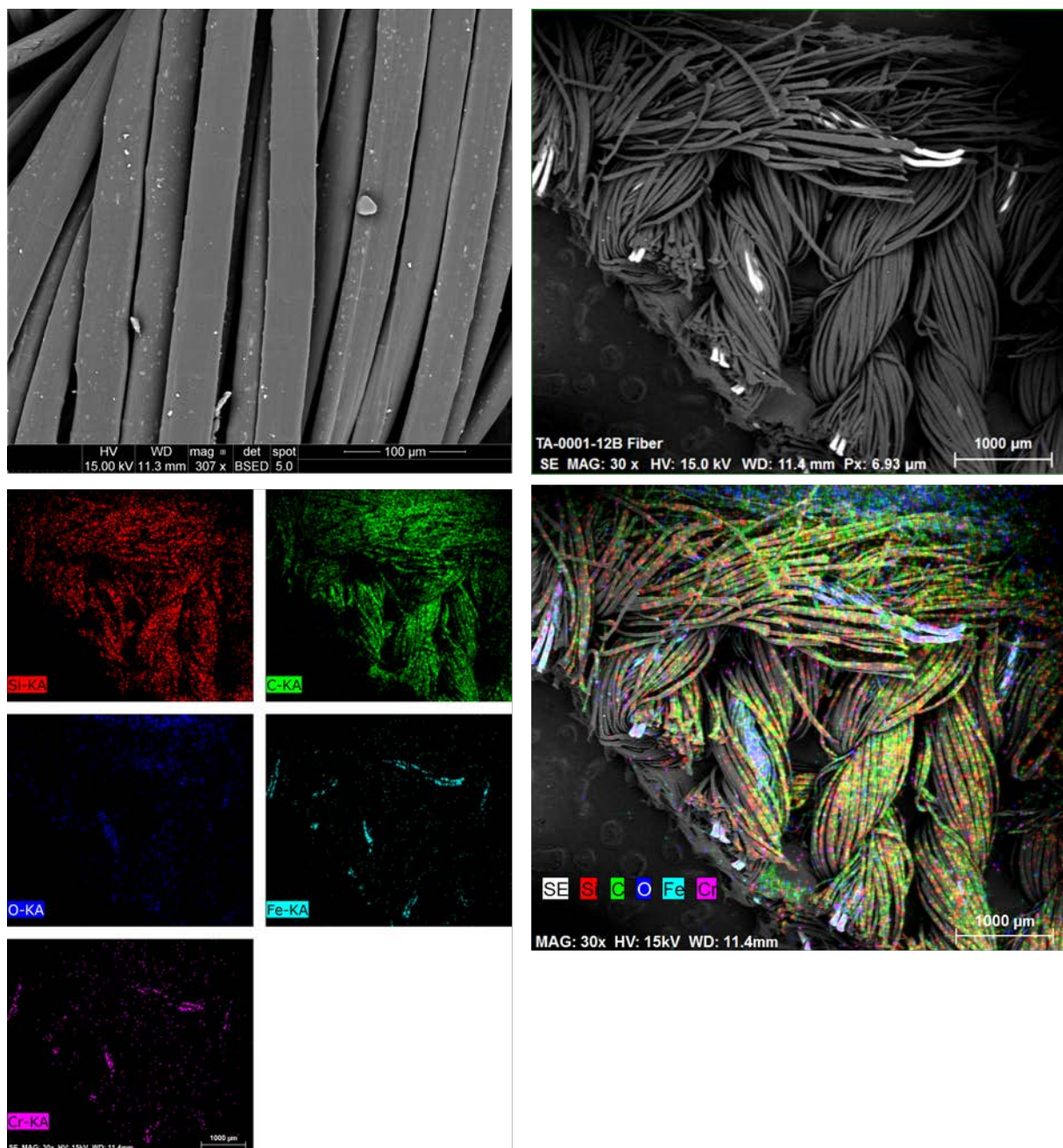
Figure 1. Glove A and Glove B fibers presented similarly (Glove B images pictured). Embedded particles (top left) and metallic wire (top right) were suggested by backscatter imaging, appearing brighter in contrast to the polymeric fiber background. Elemental analysis (bottom left and right) indicated embedded particles were silicon-based, while the wire was composed of some variety of steel.
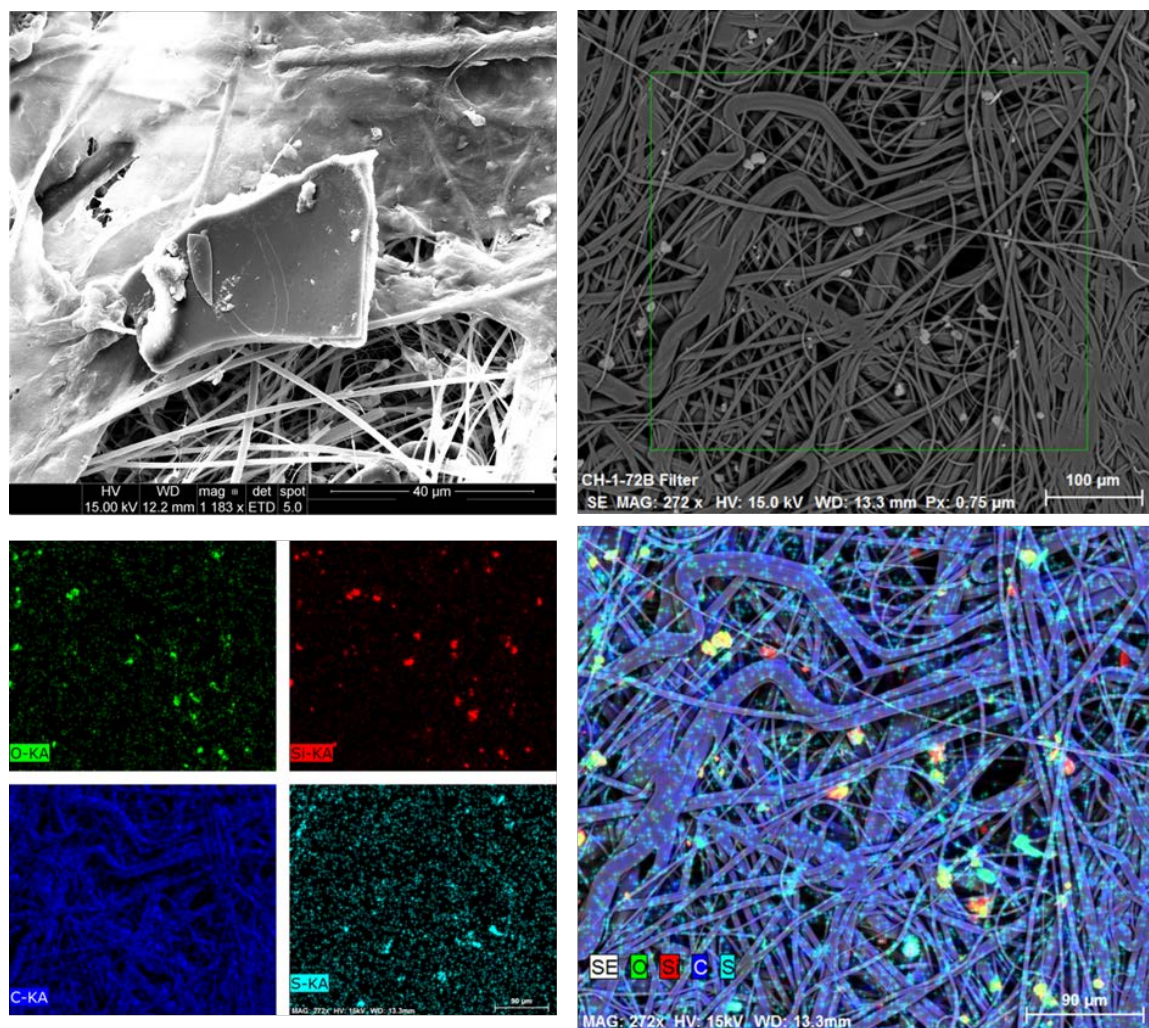
Figure 2. No evidence of graphene was identified after dissolution and filtration of Glove A and Glove B fibers. Smooth flakes measuring several layers thick were observed at intervals after complete dissolution by acid and solvent (top left), though silicon-based particles occurred at greater prevalence after acid extraction alone (remaining images). Filter material comprises the fibrous background, and sulfur signatures are thought to be reaction products of the acid extraction (not to include any graphene, which is known to be resilient to concentrated sulfuric acid at room temperature).

Glove D (Figure 3) also appeared to contain embedded particles composed of a silicon-based substance; silicon carbide was suggested by the inconsistent overlay of oxygen signatures that might indicate silicon dioxide and the lack of detection of other candidate elements. After dissolution of one variety of fiber using sulfuric acid, a second fiber variety remained that also appeared to contain embedded silicon-based particles. Further, a thinner fiber variety that EDS suggested to be composed of glass was also released.

Complete dissolution of remaining fibers using solvent appeared to release additional silicon-based particles and glass fibers (Figure 4). No other morphologies or compositions of distinction (i.e. suggestive of graphene) were observed.
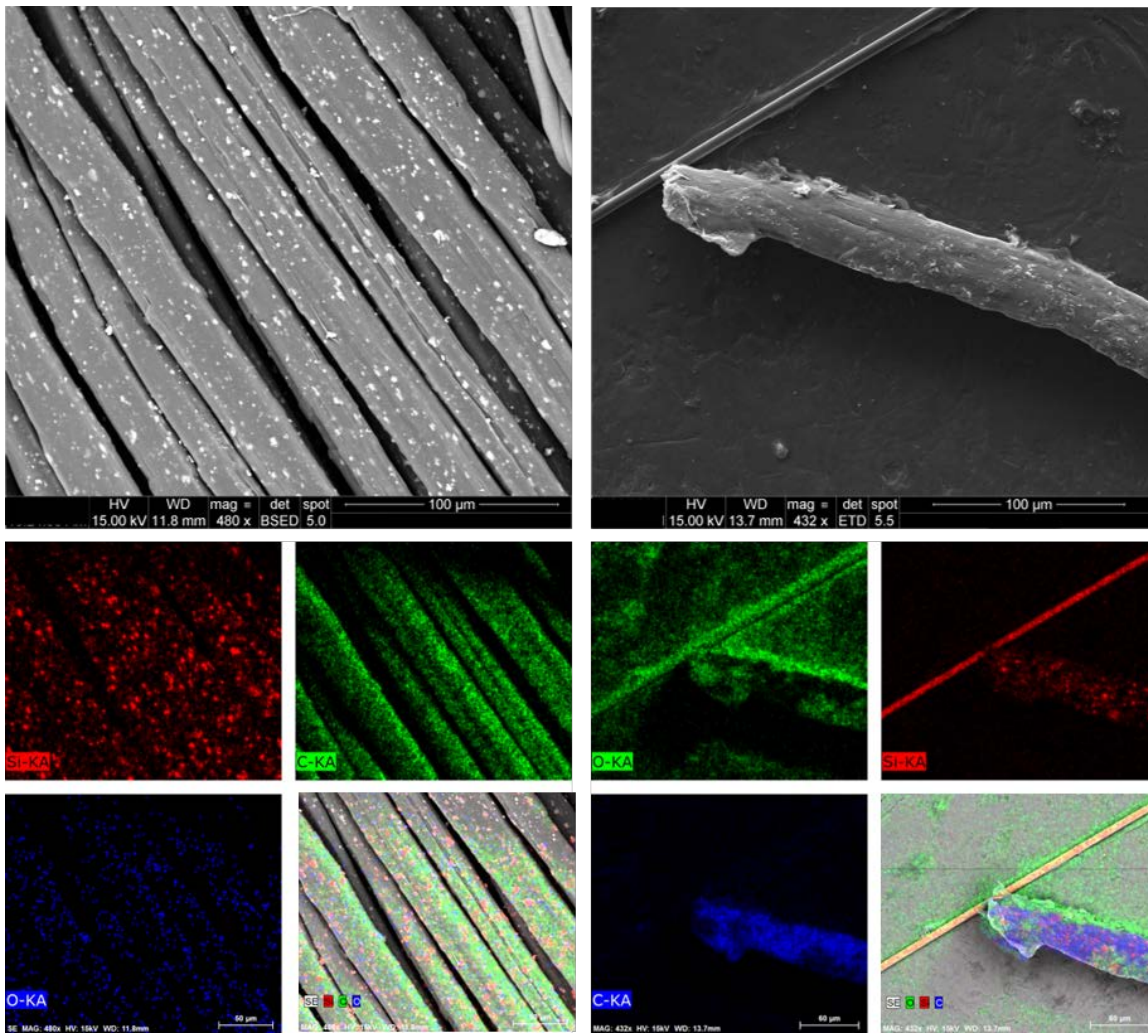
Figure 3. Glove D presented prominent embedded silicon-based particles under SEM-EDS (top left and bottom left). One variety of fiber present in the weave was dissolved by sulfuric acid, leaving a second variety of polymeric fiber with similar embedded particles as well as prolific, thinner fibers revealed by EDS to be composed of glass (top right and bottom right).
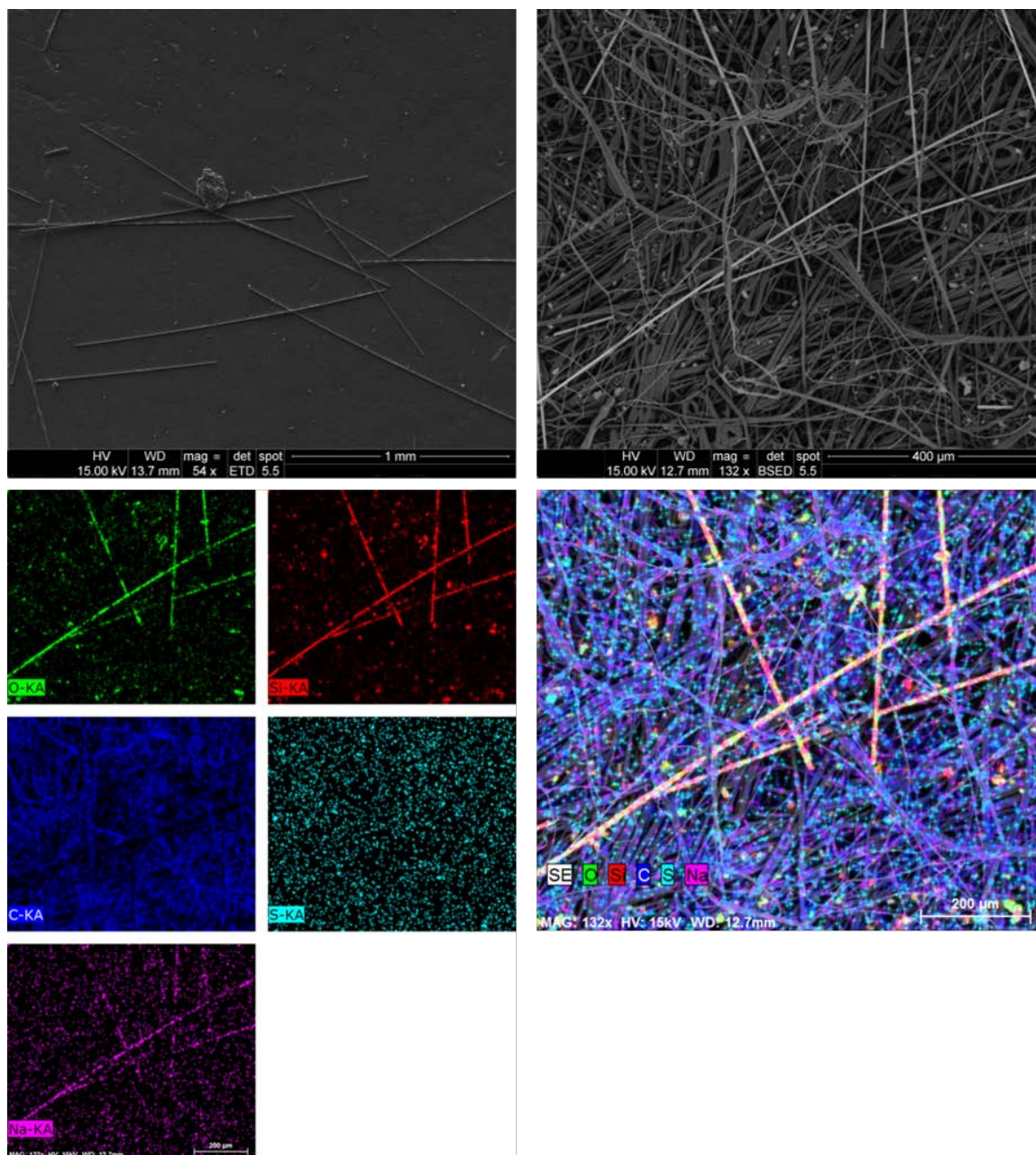
Figure 4. Complete dissolution of Glove D fibers by acid and hot solvent released prolific thin fibers and particles that were suggested by EDS to be composed of glass and a silicon-based compound, respectively.

Glove E (Figure 5) presented prolific flakey particles adhered to and partially embedded within as-received fiber surfaces. Fibers were dissolved completely in sulfuric acid (no subsequent solvent extraction was required), leaving flakey particles of varying thickness to be captured by the filter media along with accumulating redeposited polymer. No elemental signatures of particular interest were detected during EDS analysis.
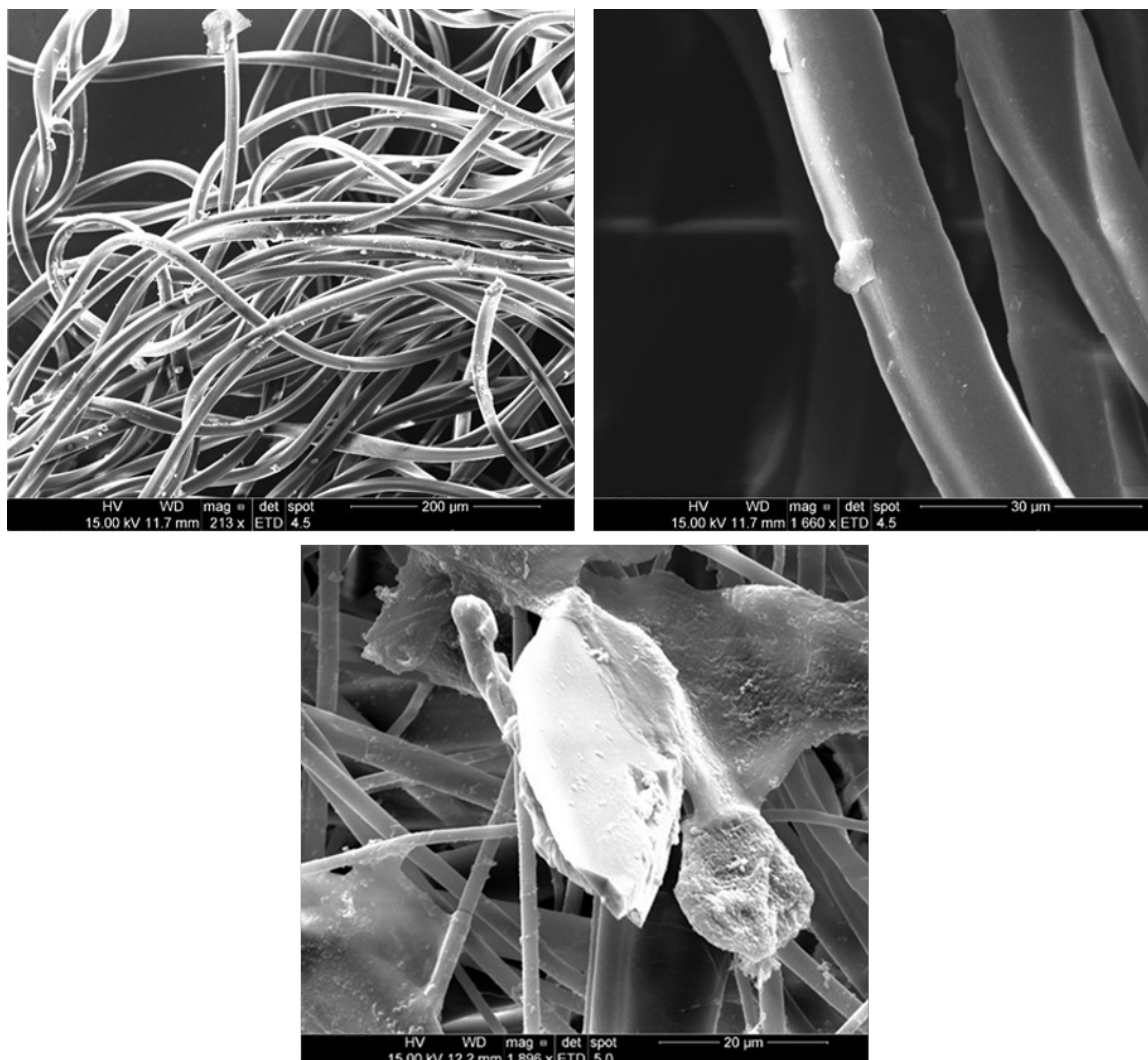

Figure 5. Glove E contained flakey particles of varying thickness that appeared to be adhered to and partially embedded in fiber surfaces (top left and top right). Upon acid extraction, flakey particles were prominently observed (bottom).

Detached thin films were observed on the glass filter substrates after hot solvent extraction of all glove samples (only required for Gloves A-D, as Glove E fibers dissolved completely during the acid extraction step). These were initially considered to be graphenic candidates during SEM analysis, but closer inspection revealed rapid susceptibility to damage by the electron beam, which would not be an expected characteristic of the highly resilient and conductive graphene. It was therefore proposed that these films were likely polymeric in nature, perhaps occurring as the hot paraffin/polymer fiber solution cooled rapidly upon contact with the glass filter substrate to form thin sheets. A corresponding investigative technique was quickly developed whereby any observed flakey particles could be sorted to determine candidacy for graphitic or graphenic composition versus polymeric origin, as demonstrated in Figure 6. Succinctly, at the working voltage of 15 keV, the film particles observed to be sheet-like at lower magnifications (and therefore prospective graphene candidates) quickly deformed when subjected to slightly higher magnifications; in fact, it was difficult to obtain images of the pristine films since the dwell time required to image was sufficient to damage the surface.
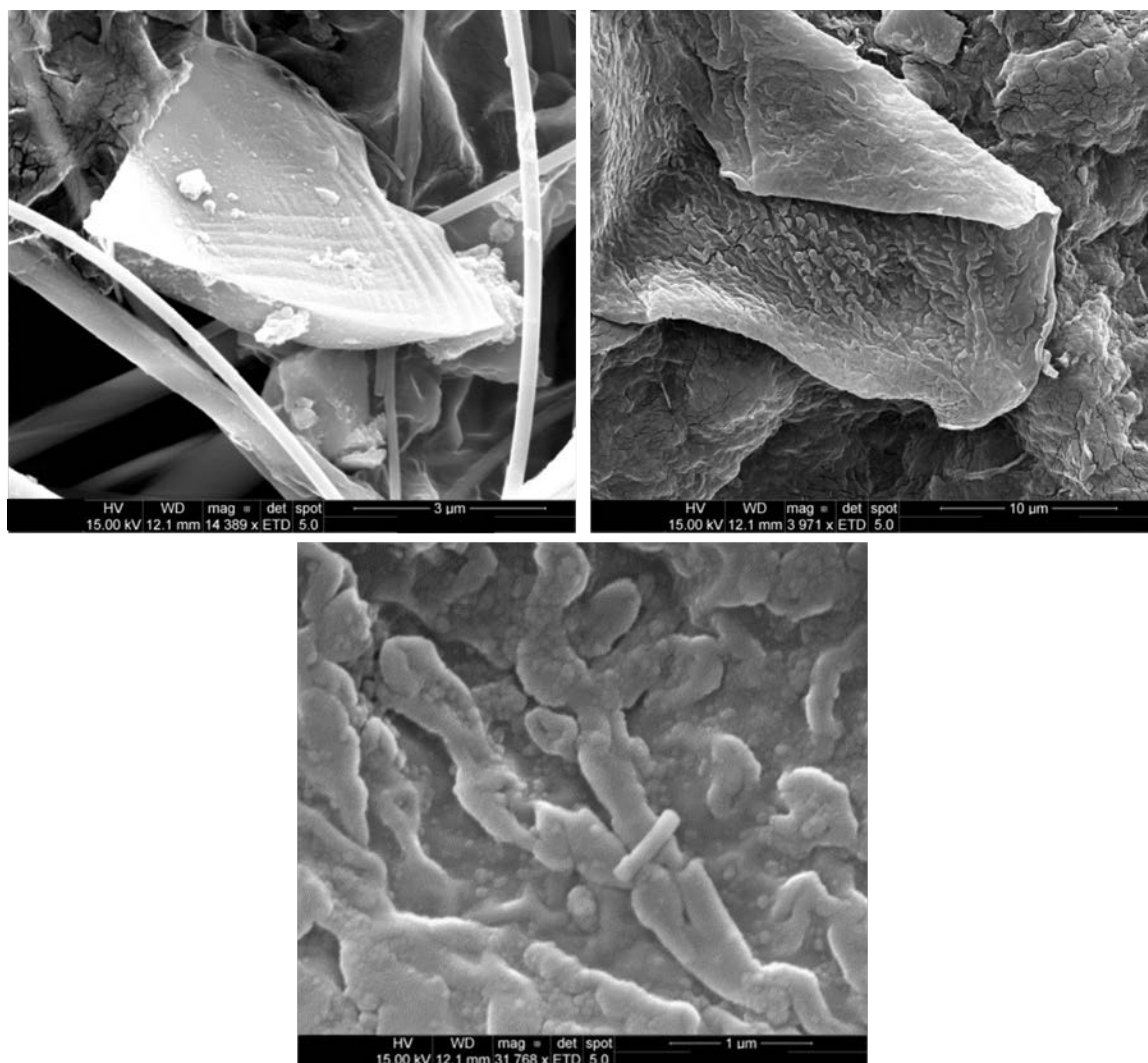
Figure 6. Flake-like particles of estimated graphitic origin were highly resistant to damage by the electron beam (top left), while films likely composed of polymer formed as hot solvent extractions cooled on the glass filter substrate were highly susceptible to damage by the electron beam (top right; higher magnification at bottom). This occurrence facilitated in-situ discernment of composition between particles of similar morphology.

3.2. Raman Spectroscopy Analysis

Raman spectroscopy performed on extracted particles rendered useful compositional information. Individual particles were identified in optical microscopy and Raman spectra acquired for these points of interest. Particles were ultimately captured after acid and solvent dissolution of the fibers using a glass filter media, which were then resuspended in ethanol by rapid stirring of the filters using methods previously described; detached portions of the glass filter media were present throughout, with particles of interest targeted for specific analysis.

A broad survey was conducted for thorough examination, seeking every opportunity to identify material of graphenic characteristic. Analyzed regions and corresponding spectra that were representative of findings during analysis of each glove are concisely presented in Figure 7.

Peaks of specific interest to this investigation were the in-plane vibrational mode G (~1580 cm^{-1}) and in-plane disorder mode D (~1350 cm^{-1}), as well as the second-order D vibration overtone, 2D (~2690 cm^{-1}) and the combination scattering peak D+G or D+D' (~2940 cm^{-1}). Traditional few-layer graphene would be expected to exhibit strong 2D peaks that exceed the G peak in magnitude, with D peak minimal in magnitude (or absent) for pristine graphene and increasing with the level of disorder[16]. As carbon layers increase toward graphite, the 2D peak shrinks in comparison to the G peak. Expansion of the carbon layers by oxygenation (in the case of graphene oxide or graphite oxide) introduces the short and broad D+D' peak[15].

As illustrated in Figure 7, many particles extracted from Glove A and Glove B exhibited Raman peaks characteristic of graphite, with 2D peaks reaching well below the magnitude of G peaks. 2D peaks were not discernibly produced by any particles extracted from Glove C or Glove D, with broad D and G peaks suggestive of amorphous carbon. Glove E particles exhibited broad D and G peaks as well as shorter, broadened 2D and D+D' (~2940 cm^{-1}) peaks which match the profiles of graphene oxide and graphite oxide.
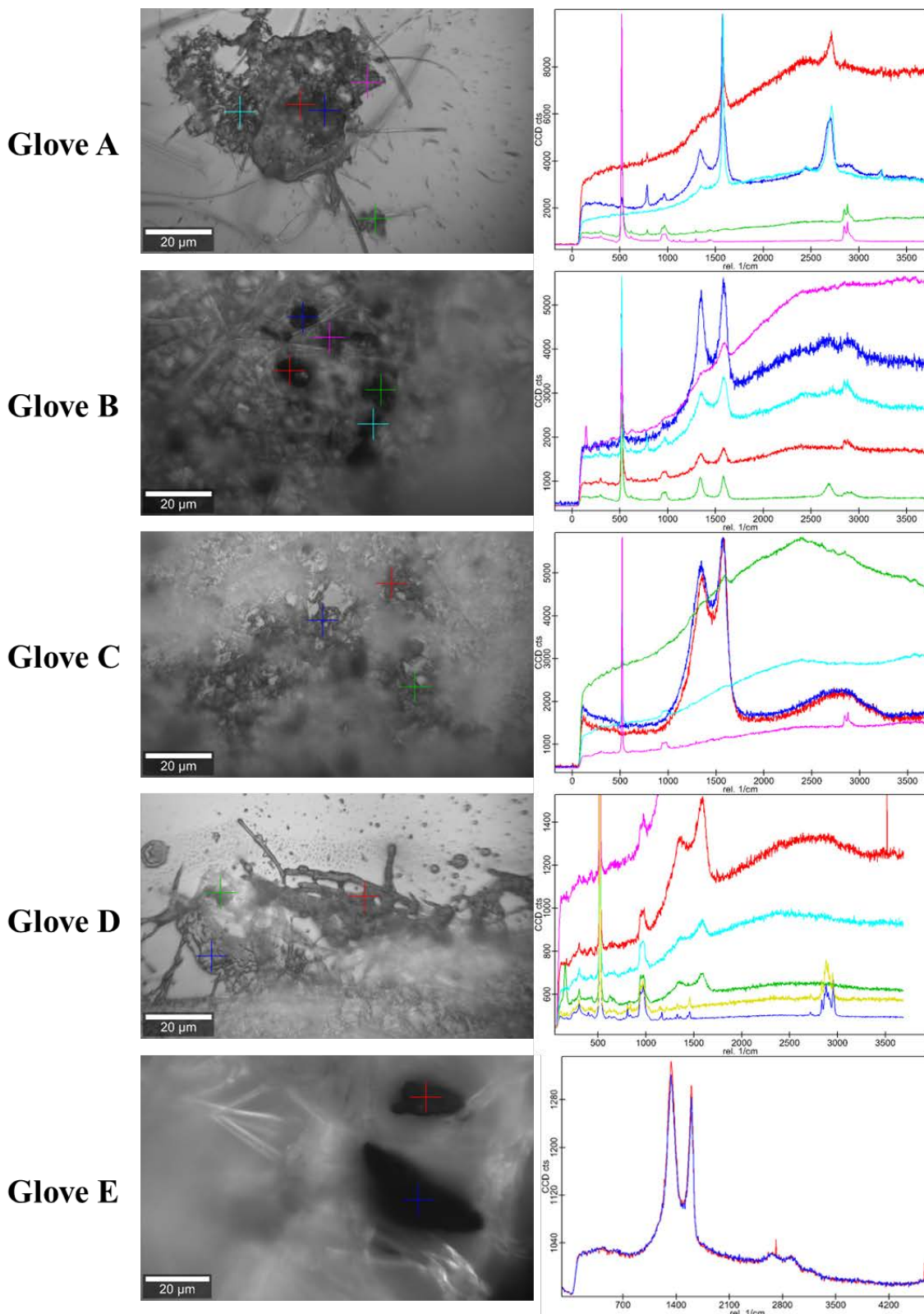
Figure 7. Raman spectra provided compositional indications for particles of interest; color-coded Raman spectra in right-hand column correspond to matching color markings in optical microscopy images in left-hand column. Glove A and Glove B exhibited peaks characteristic of graphite (blue and teal lines in Glove A spectrum and green line in Glove B spectrum), with G peaks (~1580 cm-1) far stronger than 2D peaks (~2690 cm-1). Gloves C and D only exhibited indications of amorphous carbon, with broad peaks at the D (~1350 cm-1) and G locations. Glove E exhibited peaks characteristic of graphene oxide or graphite oxide, with broad D and G peaks as well as shorter, broadened 2D and D+D' (~2940 cm-1) peaks.

4.   Discussion

Of the five gloves tested, only measurements of Glove E reasonably matched the product description, which claimed inclusion of graphene oxide. Within the scope of this experimentation as-described, no evidence of material in the graphene family was found upon investigation of Gloves A-D.

Particles extracted from Glove A and Glove B, which were from the same manufacturer, included flakes measuring several micrometers in thickness via SEM. Raman spectroscopy of similar particles, combined with the SEM-observed thickness of the flakes, strongly indicated that flakes were comprised of graphite rather than graphene.

Similarly, Glove C and Glove D (sourced from separate manufacturers) did not exhibit any indication of graphenic or even graphitic material. No morphologies that are traditionally ascribed to the graphene family were observed via SEM, and Raman spectroscopy only indicated the presence of amorphous carbon. Glove C fibers contained silicon-based particles as identified by SEM-EDS, but no other apparent additive. Glove D also contained silicon-based particles as well as a substantial amount of glass fibers.

Interestingly, while Gloves A-D were sourced from three different manufacturers, all contained fibers that included a silicon-based particle of similar characteristic, deduced to likely be composed of silicon carbide. It is possible that these glove manufacturers acquire one fiber variety from a common source. Incidentally, since other cut-inhibiting additives such as the observed silicon-based particles, steel wire, or glass fibers were indicated by SEM-EDS, it does not appear that these manufacturers relied exclusively on the inclusion of 'graphene' to impart cut-resistance.

Analysis of Glove E fibers produced immediate and unavoidable evidence of graphene oxide or graphite oxide; Raman spectra were characteristic of this composition, and observed particles were of the expected morphology. The ratio of adhered versus embedded particles within fibers was not readily apparent.

5.   Conclusions

Five cut-resistant glove products claiming graphene inclusion were sourced from four distinct manufacturers, with only one of the products exhibiting characteristics that matched the advertised inclusion of graphene oxide. Further, the established testing techniques did not discern any additional cut resistant additives in this product, whereas the other four products contained at least one non-graphenic cut-resistant additive.

It is notoriously difficult to prove a negative; it cannot be stated with absolute certainty that any of the tested products do not contain some trace level of material that could be classified in the graphene family. Under the applied methods, however, one product (Glove E) exhibited unavoidable evidence of the advertised graphene oxide content. Two products (Glove C and Glove D) did not contain any evidence of graphene or graphite content, with signatures of amorphous carbon forming the closest association. Two products (Glove A and Glove B) contained evidence of graphite flakes measuring several micrometers thick; it may be of interest to note that the manufacturer of this product has recently changed product descriptions to specifying "carbon allotrope" in place of previous assertions of "graphene" additive.

The integrity of any market depends upon consumer trust that products perform and are composed of materials as advertised. Resources are building for manufacturers (and consumers, for that matter) to ensure that the materials and products they receive meet expectations and exhibit the prescribed properties. As the graphene family market matures, it will continue to be critical that third party testing using robust analytical practices provide assurances to manufacturers and consumers while alerting parties of interest to any noncompliant products that may penetrate the market.

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