Enhancing the Strength of Acrylonitrile-Butadiene-Styrene with Gas-Phase-Synthesized Graphene for Injection-Molding Applications

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ABSTRACT

Increasing the strength-to-weight ratio of injection moldable polymers can benefit a broad range of applications, such as automobiles, aircraft, and consumer electronic devices. This report demonstrates that incorporating miniscule quantities (0.1 wt%) of gas-phase-synthesized graphene into acrylonitrile butadiene styrene (ABS) can significantly increase the strength of injection-molded specimens by over 20%. The results transform our current understanding of the structure-property relationships of graphene-filled polymer-matrix nanocomposites because highly crumpled graphene sheets with non-functionalized surfaces and nanometer-scale lateral dimensions are shown to be more effective at strengthening ABS than flat graphene flakes with functionalized surfaces and micron-scale lateral dimensions.

Graphene is a single layer of covalently bonded carbon atoms with remarkable mechanical properties that can be harnessed to strengthen polymers.[1-21] Graphene-filled polymer-matrix nanocomposites (GNCs) continue to generate extraordinary interest in the scientific community, as evidenced by the thousands of reports on the topic that were published over the last three years alone (Figure S1). Research into GNCs has been facilitated by the wide availability of graphene manufactured through the exfoliation of graphite (Figure S1), such as graphene oxide (GO), reduced graphene oxide (RGO), and graphene nanoplatelets (GNP). Therefore, our current understanding of structure-property relationships of GNCs is largely based on the results of studies on polymers containing graphene produced by top-down processes.

Enhancing the strength-to-weight ratio of acrylonitrile-butadiene-styrene (ABS) can significantly benefit society because the engineering thermoplastic is widely used in the injection molding manufacturing of automotive parts, aircraft components, and consumer electronic devices.[10-12] The mechanical properties of ABS have been enhanced by reinforcing the plastic with GO, RGO, and GNP.[6-18] However, graphene flakes derived from graphite have several drawbacks that have limited the performance of the nanomaterials in polymers, including defects, multiple graphene layers, and a propensity to aggregate and re-stack in polymer matrices.[1, 3-10, 20, 21] Exfoliating bulk graphite into graphene powder also typically requires hazardous chemicals that give rise to liquid waste that is detrimental to the environment,[1, 2, 10, 22] which makes the sustainable mass production of GNCs a challenge. High-quality and aggregation-resistant graphene sheets created through environmentally friendly processes are still needed for the large-scale manufacturing of injection-molded GNCs.

In this report, we show that gas-phase-synthesized graphene (GSG) can substantially increase the strength of injection-molded ABS. Furthermore, GSG can enhance the strength of

ABS at a much smaller filler loading relative to graphene obtained through top-down approaches. GSG is a form of graphene[23] that (1) exhibits a pure and highly ordered structure,[22] (2) consists of single-, bi-, and few-layer sheets,[22, 23] and (3) effectively disperses and resists aggregation in polymers,[24] viscous fluids,[25] and organic solvents.[23] GSG is rapidly formed without substrates by delivering ethanol directly into atmospheric pressure microwave-generated argon plasmas.[22, 23] The main byproducts of the substrate-free gas-phase synthesis process are CO and H_2,[26] which are useful gases that can be converted to fuels, lubricants, and other chemicals.[27] Therefore, high-quality and aggregation-resistant GSG could potentially enable the sustainable manufacturing of injection-molded GNCs.

GSG was incorporated into ABS using the solution compounding technique shown in Figure 1. Nanocomposites were fabricated with acetone because ABS readily dissolves in the solvent at room temperature and GSG uniformly disperses in liquid organic compounds.[23] Homogeneous mixtures consisting of GSG, acetone, and dissolved ABS were deposited onto silicone trays. Rectangular ABS-GSG sheets were created by evaporating the acetone in ambient conditions. The ABS-GSG sheets were then pelletized, dried in a vacuum oven, and injection molded into ASTM D638-14 type V specimens (Figure S2). This process was also used to produce pure ABS samples and nanocomposites consisting of ABS and commercially available GNP. Uniaxial tensile tests on pure ABS specimens, ABS containing GNP, and ABS filled with GSG (Figure S2) were performed according to the ASTM D638-14 standard. The Supporting Information (SI) provides complete details about the methods and materials that were used for fabricating, testing, and characterizing GSG-reinforced ABS-matrix nanocomposites.

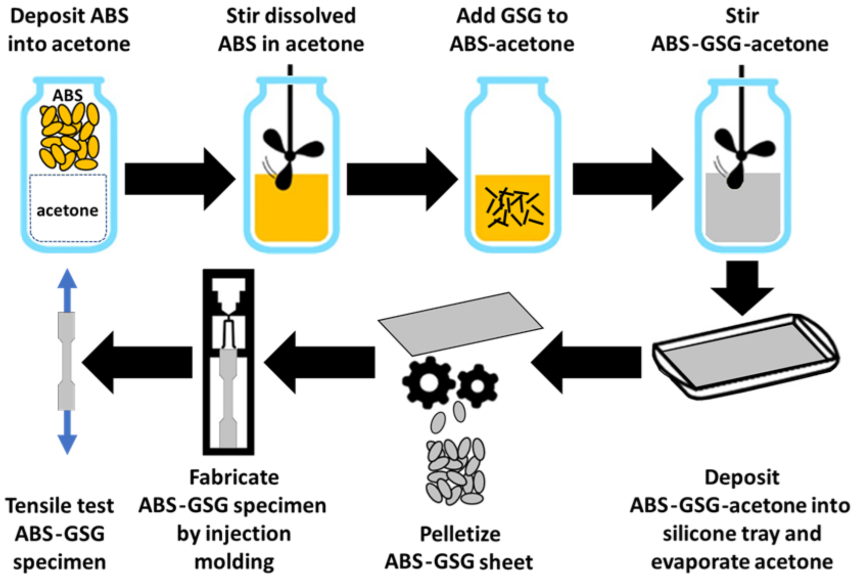

Figure 1. Schematic diagram of the process of incorporating GSG into ABS. The same process was also used to fabricate ABS and ABS-GNP specimens.

ABS-GSG nanocomposites were considerably stronger than ABS-GNP nanocomposites and pure ABS specimens. Engineering stress versus strain curves obtained from ABS, ABS-GNP, and ABS-GSG specimens are provided in Figure S3. As shown in Figure 2a, incorporating very small quantities (0.1 wt%) of GSG into ABS resulted in a significant 20.2% increase in average tensile stress relative to pure ABS. In contrast, loading ABS with 0.1 wt% GNP only caused a 4.5% change in the average tensile stress of the polymer. ABS-GSG nanocomposites exhibited an average stress at break that was 19.0% higher than pure ABS (Figure 2b), which indicates that GSG continuously reinforced ABS until the specimens fractured. The drastic increase in the strength of ABS with a GSG content of only 0.1 wt% was an unexpected result because filler loadings of at least 1.0 wt% are generally required to achieve similar improvements in ABS containing GO, RGO, or GNP.[7, 8, 11-18] The surprising strength of ABS-GSG nanocomposites motivated an investigation into the relationships between filler structure, filler-matrix interfaces, and the tensile properties of ABS-GNP and ABS-GSG nanocomposites.

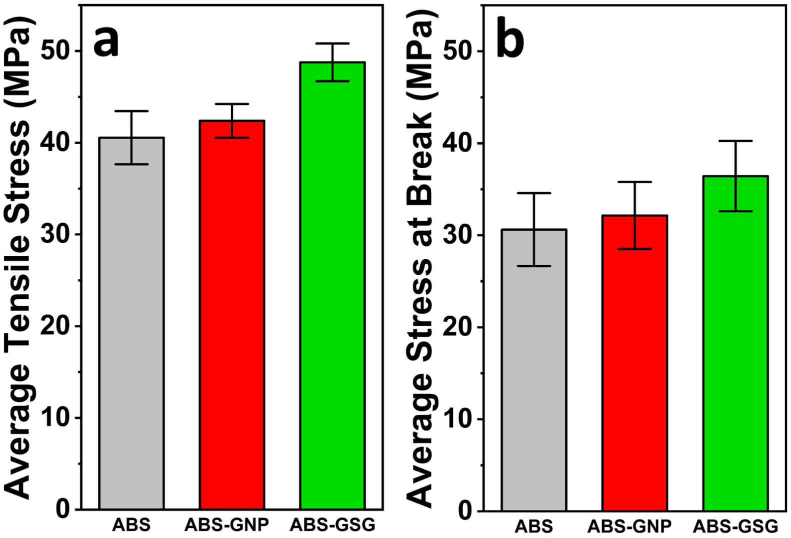

Figure 2. Tensile properties of pure ABS (gray bars) and GNCs containing GNP (red bars) and GSG (green bars). (a) Average tensile stress of ABS, ABS-GNP, and ABS-GSG specimens. (b) average stress at break of the specimens. Standard deviation bars are shown.

Based on the current knowledge of GNCs, the effective support of polymers by graphene requires atomically-thin flakes with micron-scale lateral dimensions, high aspect ratios (lateral size divided by thickness), and highly ordered structures.[1, 4-7, 18-21] The scanning electron microscopy (SEM) image of the GNP used in this study (Figure 3a) shows that the flakes were several microns in size. In contrast, the GSG powder incorporated into ABS consisted of sheets that were much smaller than GNP (Figure 3b). The thinness of GNP enables the underlying lacey carbon film to be visible in the transmission electron microscopy (TEM) image shown in Figure 3c, which reveals the relatively high aspect ratio of the flakes. The TEM image of GSG (Figure 3d) shows that the sheets are also nearly transparent but have lateral dimensions on the order of hundreds of nanometers. Thus, the GSG sheets utilized in our experiments had a much lower aspect ratio than GNP flakes. The Raman spectra of GNP (Figure 3e) and GSG (Figure 3f) demonstrate that structural disorder might not have factored into the property differences between ABS-GNP and ABS-GSG specimens. GNP and GSG have a G peak at ~1560 cm^{-1}, which shows that both fillers consist of graphene.[28] A D peak at ~1340 cm^{-1} that is caused by defects and disorder in graphene sheets[28] is also present in the Raman spectra of GNP and GSG. The intensity ratio of the D and G peaks (I_D/I_G) can be used to assess the quality of the nanomaterials because I_D/I_G becomes higher as the level of disorder in graphene increases.[28] GNP had an I_D/I_G of ~0.1 (Figure 3e) while GSG had an I_D/I_G of ~0.3 (Figure 3f), which suggests that the GNP had a lower degree of disorder than GSG. However, the edges of graphene sheets generate D peaks in Raman spectroscopy[28] and the large number of GSG edges detected by the Raman spectrometer may have increased the I_D/I_G of the nanomaterial. GNP flakes exhibited higher aspect ratios and similar (or better) structural quality than GSG sheets, but the average tensile stress of GNP-reinforced ABS was much lower than ABS containing GSG. The results indicate that the dissimilar mechanical properties of ABS-GNP and ABS-GSG nanocomposites could have been a result of three key differences between GNP and GSG: thickness, flatness, and graphitic nanocrystals.

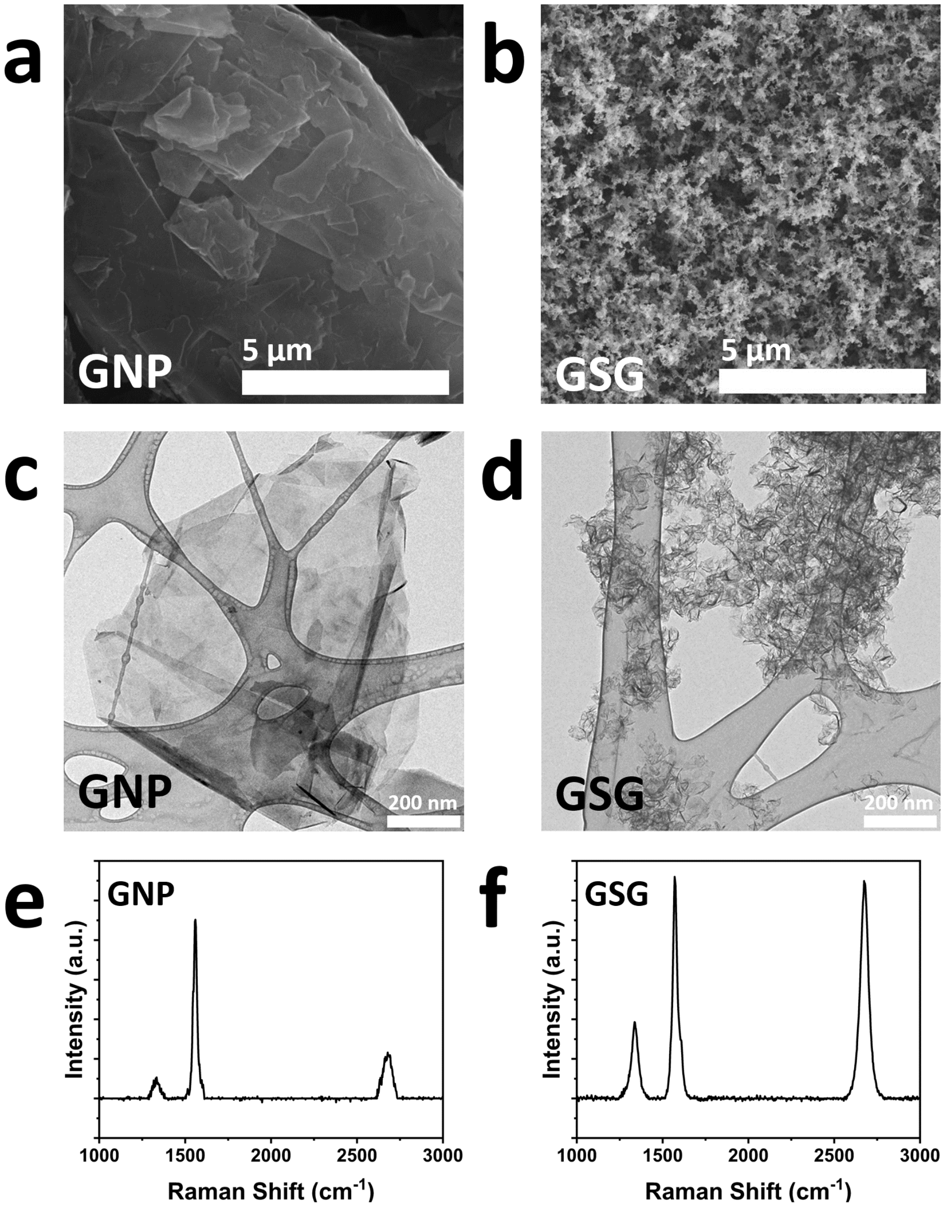

Figure 3. Electron microscopy and Raman spectroscopy characterization of the GNP and GSG incorporated into ABS. (a, b) SEM images of GNP and GSG, respectively. Scale bars are 5 µm. (c, d) TEM images of lacey carbon films supporting GNP and GSG, respectively. Scale bars are 200 nm. (e, f) Raman spectra of GNP and GSG, respectively.

The thicknesses of GNP and GSG might have impacted the mechanical properties of the ABS specimens containing these nanomaterials. The clearest discrepancy between the Raman spectra of GNP and GSG is the 2D peak located at ~2680 cm^{-1}, which indicates the number of layers in graphene.[28] As shown in Figure 3f, GSG exhibited a sharp 2D peak and the intensity ratio of the 2D and G peaks (I_{2D}/I_G) was ~1.0, which demonstrates that the filler mainly consisted of sheets with fewer than three graphene layers.[28] The GNP flakes had an I_{2D}/I_G of ~0.3 (Figure 3e), which shows that the powder consisted of nanoplatelets with more than five graphene layers.[28] TEM images of filler-matrix interfaces in the GNC specimens elucidate the effect of filler thickness on specimen deformation. The low-magnification TEM image of GNP in ABS (Figure 4a) shows that that the nanoplatelets were completely encased in the plastic. Despite being highly crumpled, GSG was also fully encapsulated in ABS (Figure 4b). The high-magnification TEM image of the ABS-GNP interface (Figure 4c) suggests that ABS was mainly in contact with the outer surfaces of the GNP flakes. Polymer chains did not appear to penetrate the spaces between the individual layers of GNP, as evidenced by the 0.34 nm interlayer spacing throughout the nanoplatelet that is characteristic of multi-layer graphene.[21] Indeed, the thickness of graphene can affect the properties of GNCs.[3-5, 19-21] For multi-layer nanoplatelets in a polymer, applied stresses to the matrix are transmitted to the outer surfaces of the filler, which causes the sliding of the graphene layers within the flakes.[3-5, 19-21] In contrast, a high magnification TEM image of the GSG-ABS interface (Figure 4d) shows that the much thinner sheets are nearly invisible in ABS. Folded and crumpled regions in the GSG sheets are the most visible features in the image. Relative to GNP, there are fewer layers in GSG that can experience sliding during the deformation of ABS. GSG powder also contains highly ordered single-layer graphene[22, 23] that can provide optimal reinforcement to a polymer matrix.[4, 5, 20, 21] Therefore, the thinness of GSG may have played a role in the stronger ABS-GSG nanocomposites.

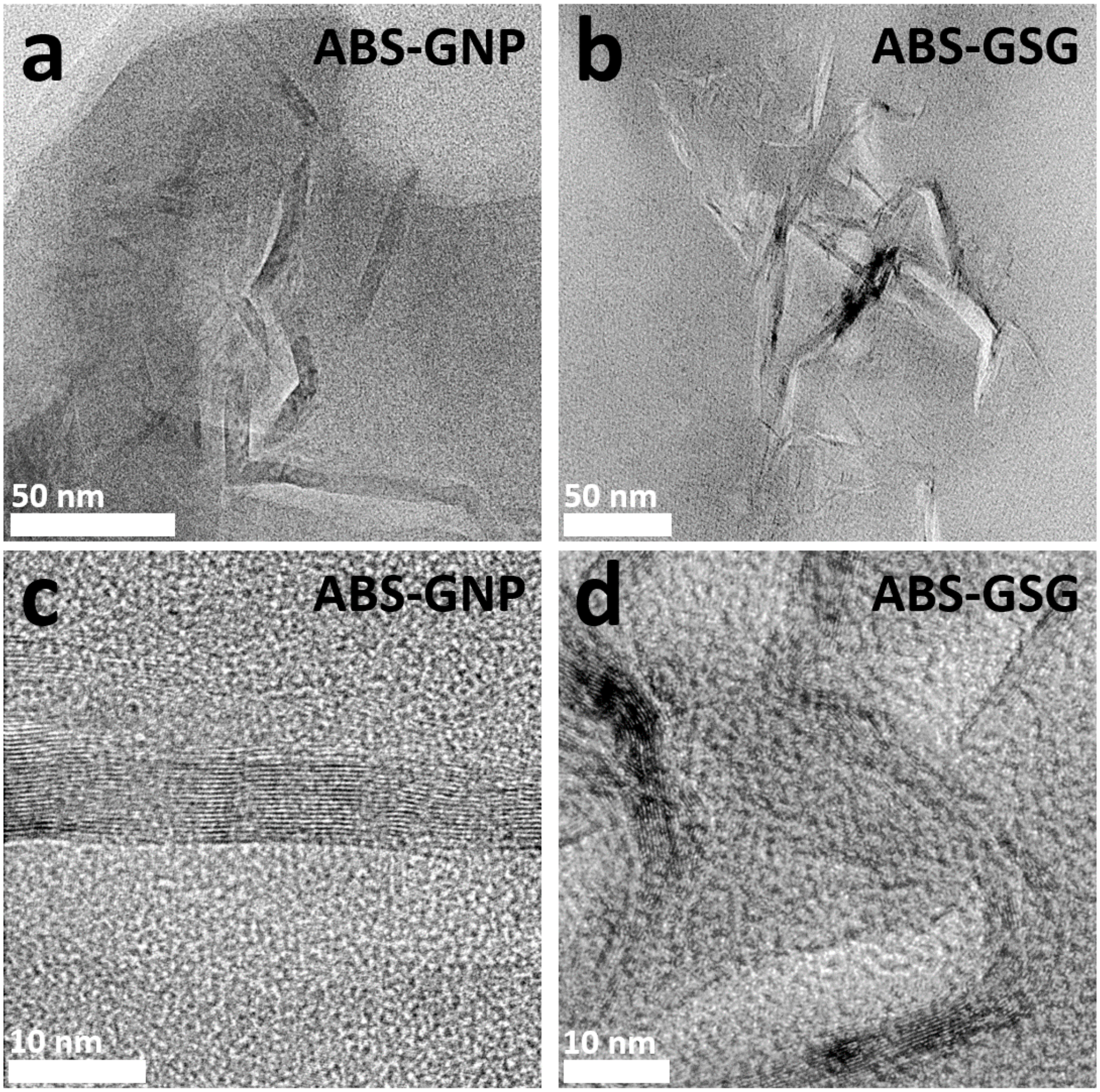

Figure 4. TEM images of filler-matrix interfaces in ABS-matrix nanocomposites containing GNP and GSG. (a, b) Low-magnification TEM images of ABS containing GNP and GSG, respectively. Scale bars are 50 nm. (c, d) High-magnification TEM images of ABS containing GNP and GSG, respectively. Scale bars are 10 nm.

The highly crumpled structure of GSG could also be contributing to the enhanced strength of the ABS-GSG specimens. For few-layer graphene with outer surfaces in complete contact with a polymer, the sliding of individual layers has been shown to be more challenging in wrinkled sheets than in flat flakes.[3, 19] The crumples of bilayer and few-layer GSG could have hindered the sliding of individual graphene sheets when forces were transferred from ABS to the filler. Additionally, the movement of polymer chains around GSG may have been impeded by crumples in the sheets. Studies into ABS-matrix GNCs has shown that chemical surface treatments to bind ABS to the surfaces of graphene can increase the mechanical properties of the nanocomposites.[7, 10-13, 16, 17] Unimpeded movements of unbound polymer chains around flat and non-functionalized GNP flakes could explain the marginal reinforcement of ABS by GNP. GSG also does not have functionalities that can bind polymer chains to its surface because it has a mass composition of 98.9% C and 1.0% H.[22] The movement of polymer chains around the many crumples of GSG may have required higher applied forces than in flat GNP flakes. Thus, the dissimilar mechanical properties of ABS-GSG and ABS-GNP specimens could have arisen from differences in the sliding of individual graphene layers and the movement of polymer chains in the nanocomposites.

The dispersibility and aggregation-resistance of crumpled GSG in ABS may have also been a factor in the enhanced mechanical properties of ABS-GSG specimens. The aggregation of graphene sheets in polymers can create failure points in nanocomposites.[20] Furthermore, flat platelets can re-stack into graphite due to van der Waals forces,[2-6, 20, 21] which prevents polymer chains from interfacing with individual graphene layers.[20] Strategies for mitigating the aggregation and re-stacking of graphene in ABS include the use of surface treatments,[7, 10-13, 16] rod-shaped fillers,[8, 18] and dopants.[14] The GNP flakes used in this study were unmodified. As a result, the aggregation and re-stacking of GNP in dissolved ABS might have occurred during the acetone evaporation step of the nanocomposite fabrication process. The deliberate crumpling of graphite-derived graphene has improved the dispersion of the nanomaterial in fluids and has prevented the re-stacking of individual sheets.[29] Therefore, the uniform distribution of highly crumpled GSG sheets in ABS could have played a role in the observed strength enhancements in ABS-GSG nanocomposites.

Graphitic nanocrystals that are inherent to GSG might have also contributed to the relatively high tensile stress of ABS-GSG nanocomposites. Experiments aimed at mechanically manipulating GSG have revealed that graphitic nanocrystals in GSG enable the sheets to reversibly deform and resist flattening when forces are applied to the nanomaterial.[30] The graphitic nanocrystals maintain the crumpled morphology of GSG and cause the sheets to behave like springs. The presence of graphitic nanocrystals in GNP flakes has not been reported. Thus, the spring-like restoring forces of graphitic nanocrystals in GSG are another possible root cause of the differences in strength between ABS-GSG and ABS-GNP specimens.

In conclusion, the enhanced strength of ABS-GSG nanocomposites could be a result of a synergistic combination of the thinness, crumpled morphology, and graphitic nanocrystals of GSG. The results presented here justify further research into GSG-reinforced plastics. For instance, the effect of higher GSG content on the strength of ABS remains unknown. Filler aggregation has limited the optimal loading of graphene produced by top-down processes to below 5 wt% in ABS.[7, 9, 10, 15, 18] GSG resists aggregation, which could enable the continuous strengthening of ABS as the amount of GSG is increased. The melt mixing of GSG and ABS can also be performed to determine if the observed results are due to the acetone dissolution approach. Methods of crumpling graphene derived from graphite have been developed,[29] and the impact of sheet thickness and graphitic nanocrystals on the strength of ABS may be assessed by filling the plastic with deliberately crumpled graphene obtained through top-down processes.

The electrical and thermal conductivities of ABS-GSG nanocomposites should also be measured because interlocking GSG sheets could create electrically and thermally conductive pathways in polymers. Importantly, GSG should also be compounded with other plastics to ascertain if similar property enhancements occur in other thermoplastic matrices. Nevertheless, this report advances our current understanding of structure-property relationships of GNCs and demonstrates a potential avenue toward the sustainable injection molding manufacturing of strong and lightweight nanocomposites.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge at https://pubs.acs.org/doi/.

> A brief description of publications on graphene-filled polymer-matrix nanocomposites, which are summarized in Figure S1. Additional experimental details, materials, and methods of the nanocomposite fabrication process, as well as Figure S2, which shows an injection-molded ABS-matrix nanocomposite containing GSG. A description of the tensile testing procedure and Figure S3, which shows engineering stress vs. strain curves obtained from pure ABS specimens, ABS-GNP nanocomposites, and ABS-GSG nanocomposites. Descriptions of SEM, TEM, and Raman spectroscopy. (PDF)

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Author Contributions

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

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Majumder, S.; Meher, A.; Moharana, S.; Kim, K. H. Graphene nanoribbon synthesis and properties in polymer composites: A review. *Carbon* **2024,** *216*, 26.

(2) Yadav, S.; Raman, A. P. S.; Meena, H.; Goswami, A. G.; Bhawna; Kumar, V.; Jain, P.; Kumar, G.; Sagar, M.; Rana, D. K.; Bahadur, I.; Singh, P. An Update on Graphene Oxide: Applications and Toxicity. *ACS Omega* **2022**, *7* (40), 35387-35445.

(3) Chen, H.; Zhuo, F. L.; Zhou, J.; Liu, Y.; Zhang, J. B.; Dong, S. R.; Liu, X. Q.; Elmarakbi, A.; Duan, H. G.; Fu, Y. Q. Advances in graphene-based flexible and wearable strain sensors. *Chem. Eng. J.* **2023,** *464*, 25.

(4) Ibrahim, A.; Klopocinska, A.; Horvat, K.; Hamid, Z. A. Graphene-Based Nanocomposites: Synthesis, Mechanical Properties, and Characterizations. *Polymers-Basel* **2021,** *13* (17), 32.

(5) Zhang, Z. Y.; Du, J. G.; Li, J. X.; Huang, X. D.; Kang, T.; Zhang, C.; Wang, S.; Ajao, O. O.; Wang, W. J.; Liu, P. W. Polymer nanocomposites with aligned two-dimensional materials. *Prog. Polym. Sci.* **2021,** *114*, 31.

(6) Trivedi, D. N.; Rachchh, N. V. Graphene and its application in thermoplastic polymers as nano-filler- A review. *Polymer* **2022,** *240*, 124486.

(7) George, E.; Joy, J.; Anas, S. Acrylonitrile-based polymer/graphene nanocomposites: A review. *Polym. Composite* **2021,** *42* (10), 4961-4980.

(8) Ceretti, D. V. A.; Fiorio, R.; Van Waeleghem, T.; Desmet, A.; Florizoone, B.; Cardon, L.; D'Hooge, D. R. Exploiting mono- and hybrid nanocomposite materials for fused filament fabrication with acrylonitrile butadiene styrene as polymer matrix. *J. Appl. Polym. Sci.* **2022,** *139* (41), 21.

(9) Chandra, R. B. J.; Shivamurthy, B.; Kumar, M. S.; Prabhu, N. N.; Sharma, D. Mechanical and Electrical Properties and Electromagnetic-Wave-Shielding Effectiveness of Graphene-Nanoplatelet-Reinforced Acrylonitrile Butadiene Styrene Nanocomposites. *J. Compos. Sci.* **2023,** *7* (3), 19.

(10) Lee, S. J.; Baek, J.; Jeon, I.-Y. Preparation and characteristics of decene-functionalized graphitic nanoplatelets/acrylonitrile butadiene styrene hybrid nanocomposites. *Polymer* **2024,** *294*, 126727.

(11) Huang, G. B.; Chen, W.; Wu, T.; Guo, H. C.; Fu, C. Y.; Xue, Y. J.; Wang, K.; Song, P. A. Multifunctional graphene-based nano-additives toward high-performance polymer nanocomposites with enhanced mechanical, thermal, flame retardancy and smoke suppressive properties. *Chem. Eng. J.* **2021,** *410*, 12.

(12) Chen, X. B.; Lu, S. L.; Sun, C. F.; Song, Z. B.; Kang, J.; Cao, Y. Exploring Impacts of Hyper-Branched Polyester Surface Modification of Graphene Oxide on the Mechanical Performances of Acrylonitrile-Butadiene-Styrene. *Polymers-Basel* **2021,** *13* (16), 12.

(13) Huang, G. B.; Huo, S. Q.; Xu, X. D.; Chen, W.; Jin, Y. X.; Li, R. R.; Song, P. A.; Wang, H. Realizing simultaneous improvements in mechanical strength, flame retardancy and smoke suppression of ABS nanocomposites from multifunctional graphene. *Compos. Part B-Eng.* **2019,** *177*, 10.

(14) Panwar, V.; Pal, K. Influence of addition of selective metallic species on mechanical properties of graphene/acrylonitrile-butadiene-styrene composites. *Polym. Composite* **2020,** *41* (4), 1636-1648.

(15) Gao, A. L.; Zhao, F. W.; Wang, F.; Zhang, G. F.; Zhao, S.; Cui, J.; Yan, Y. H. Highly conductive and light-weight acrylonitrile-butadiene-styrene copolymer/reduced graphene nanocomposites with segregated conductive structure. *Compos. Part A-Appl. S.* **2019,** *122*, 1-7.

(16) Huang, G. B.; Han, D. M.; Jin, Y. X.; Song, P. G.; Yan, Q. D.; Gao, C. Fabrication of Nitrogen-Doped Graphene Decorated with Organophosphor and Lanthanum toward High-Performance ABS Nanocomposites. *ACS Appl. Nano Mater.* **2018,** *1* (7), 3204-3213.

(17) Panwar, V.; Pal, K. An optimal reduction technique for rGO/ABS composites having high-end dynamic properties based on Cole-Cole plot, degree of entanglement and C-factor. *Compos. Part B-Eng.* **2017,** *114*, 46-57.

(18) Jyoti, J.; Babal, A. S.; Sharma, S.; Dhakate, S. R.; Singh, B. P. Significant improvement in static and dynamic mechanical properties of graphene oxide-carbon nanotube acrylonitrile butadiene styrene hybrid composites. *J. Mater. Sci.* **2018,** *53* (4), 2520-2536.

(19) Androulidakis, C.; Koukaras, E. N.; Rahova, J.; Sampathkumar, K.; Parthenios, J.; Papagelis, K.; Frank, O.; Galiotis, C. Wrinkled Few-Layer Graphene as Highly Efficient Load Bearer. *ACS Appl. Mater. Inter.* **2017,** *9* (31), 26593-26601.

(20) Papageorgiou, D. G.; Kinloch, I. A.; Young, R. J. Mechanical properties of graphene and graphene-based nanocomposites. *Prog. Mater. Sci.* **2017,** *90*, 75-127.

(21) Young, R. J.; Kinloch, I. A.; Gong, L.; Novoselov, K. S. The mechanics of graphene nanocomposites: A review. *Compos. Sci. Technol.* **2012,** *72* (12), 1459-1476.

(22) Dato, A. Graphene synthesized in atmospheric plasmas—A review. *J. Mater. Res.* **2019,** *34* (1), 214-230.

(23) Dato, A.; Radmilovic, V.; Lee, Z.; Phillips, J.; Frenklach, M. Substrate-free gas-phase synthesis of graphene sheets. *Nano Lett.* **2008,** *8* (7), 2012-6.

(24) Nakahara, K.; Knego, J.; Sloop, T.; Bisquera, C.; Subler, N.; Dato, A. Enhanced mechanical properties of epoxy-matrix nanocomposites reinforced with graphene synthesized in atmospheric plasmas. *Plasma Process. Polym.* **2020,** *17* (5), 1900244.

(25) Krauss, G. G.; Dato, A.; Siniawski, M. Enhanced lubricating properties of oils containing graphene synthesized in atmospheric plasmas. *Carbon Trends* **2020,** *1*, 100010.

(26) Rincón, R.; Melero, C.; Jiménez, M.; Calzada, M. D. Synthesis of multi-layer graphene and multi-wall carbon nanotubes from direct decomposition of ethanol by microwave plasma without using metal catalysts. *Plasma Sources Sci. T.* **2015,** *24* (3), 032005.

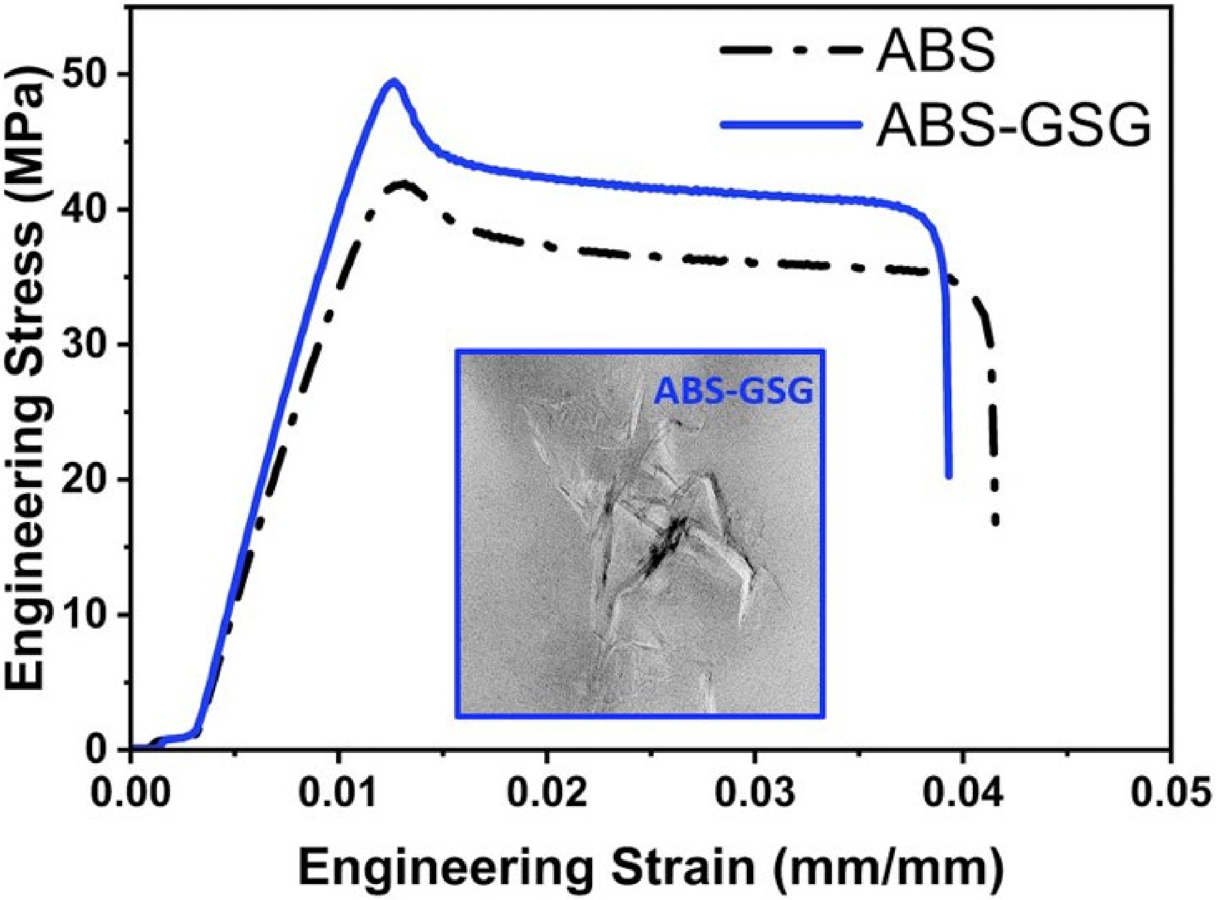
(27) Pham, T. T. P.; Ro, K. S.; Chen, L.; Mahajan, D.; Siang, T. J.; Ashik, U. P. M.; Hayashi, J.-i.; Pham Minh, D.; Vo, D.-V. N. Microwave-assisted dry reforming of methane for syngas production: a review. *Environ. Chem. Lett.* **2020,** *18* (6), 1987-2019.

(28) Wu, J. B.; Lin, M. L.; Cong, X.; Liu, H. N.; Tan, P. H. Raman spectroscopy of graphene-based materials and its applications in related devices. *Chem. Soc. Rev.* **2018,** *47* (5), 1822-1873.

(29) Luo, J.; Jang, H. D.; Sun, T.; Xiao, L.; He, Z.; Katsoulidis, A. P.; Kanatzidis, M. G.; Gibson, J. M.; Huang, J. Compression and aggregation-resistant particles of crumpled soft sheets. *ACS Nano* **2011,** *5* (11), 8943-9.

(30) Lin, A. Y. W.; Yu, X.-x.; Dato, A.; Krauss, G.; Marks, L. D. In situ observations of graphitic staples in crumpled graphene. *Carbon* **2018,** *132*, 760-765.

TABLE OF CONTENTS (TOC)/ABSTRACT GRAPHIC



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Supporting Information

Enhancing the Strength of Acrylonitrile-Butadiene-Styrene with Gas-Phase-Synthesized Graphene for Injection-Molding Applications

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S1. Brief Summary of Publications on Graphene-Filled Polymer-Matrix Nanocomposites

A search of Web of Science (https://www.webofscience.com) using "Graphene (Topic) and Polymer (Topic) and Nanocomposite (Topic)" generates 7,549 results between the years 2005 and 2023. As shown in Figure S1, over one third of the results (2,613) were published between the years 2021 and 2023 alone. Figure S1 also shows that refining the search with "Graphene (Topic) and Polymer (Topic) and Nanocomposites (Topic) and Graphene Oxide (Topic)" or "Graphene (Topic) and Polymer (Topic) and Nanocomposites (Topic) and Graphene Nanoplatelets (Topic)" demonstrates that the current understanding of structure-property relationships in graphene-filled polymer-matrix nanocomposites is largely based on the results of studies on polymers containing graphene produced through the top-down exfoliation of graphite.

S2. Methods and Materials

Graphene was synthesized without substrates in the gas phase by delivering ethanol (Sigma-Aldrich 200 proof, HPLC/spectrophotometric grade) directly into atmospheric pressure argon plasmas using a commercially-available microwave (2.45 GHz) plasma reactor (MKS/ASTeX AX2518). Argon gas was passed through a quartz tube (21 mm internal diameter) into the reactor at a rate of 1.71 L/min to ignite and sustain argon plasmas at an applied microwave forward power of 250 W. A jet nebulizer (Respironics HS860) was used to create an aerosol consisting of argon gas (2 L/min) and ethanol droplets (2×10^{-4} L/min). A smaller alumina tube (3 mm internal diameter) that was located within the quartz tube was used to pass aerosols directly into argon plasmas. Gas-phase-synthesized graphene (GSG) powder was collected downstream from the plasma on membrane filters (Pall Nylaflo membrane disc filters, 0.42 µm pore size). The GSG used in this study was procured by gently scraping the powder from filters using a laboratory spatula.

GSG was incorporated into acrylonitrile butadiene styrene (ABS) purchased from Premier Plastic Resins (PPR-ABS02-B). A solution compounding process was used to mix GSG and ABS in acetone (Sigma-Aldrich ACS reagent ≥ 99.5%). First, ABS was dissolved in acetone (0.3 g of ABS per mL of acetone) using an overhead mechanical mixer (XZBELEC DX-120D) operating at 450 rpm for 1 hour. The dissolved ABS in acetone was then blended with 0.1 wt% GSG at 450 rpm for six hours. ABS-GSG-acetone mixtures were then deposited in silicone trays and ABS-GSG nanocomposite sheets were created by evaporating the acetone at ambient conditions for 24 hours. A Filabot Reclaimer was then used to pelletize the nanocomposite sheets. The nanocomposite pellets were dried in an oven at 80 ºC for 8 hours. As shown in Figure S2, the dried pellets were injection molded into ASTM D638-14 Type V test specimens using a plastic injection molding machine (Morgan Industries, Inc. G-125T) and custom injection molds. The same process was used to fabricate pure ABS test specimens and ABS-matrix nanocomposites containing 0.1 wt% graphene nanoplatelets (GNP) purchased from Graphene Supermarket (SKU-NP-8NM-5G).

S3. Tensile Testing of ABS, ABS-GNP Nanocomposites, and ABS-GSG Nanocomposites

An INSTRON 3343 equipped with a 1 kN load cell was used to perform uniaxial tensile tests on fabricated specimens according to the ASTM D638-14 standard. Figure S3 shows engineering stress versus engineering strain curves for specimens composed of pure ABS (n = 13), ABS and 0.1 wt% GNP (n = 11), and ABS and 0.1 wt% GSG (n = 16).

S4. Characterizing Fillers and Nanocomposites

Scanning electron microscopy and transmission electron microscopy were performed at the Central Facility for Advanced Microscopy and Microanalysis at UC Riverside. Scanning electron microscopy images of GNP and GSG were taken using a ThermoFisher Scientific NNS450. A 120 kV Tecnai 12 transmission electron microscope was used to obtain images of GNP and GSG. Images of filler-matrix interfaces in ABS-GNP and ABS-GSG nanocomposites were taken using a ThermoFisher Scientific Titan Themis 300 operating at 300 kV. Raman spectroscopy was performed on silicon covered with GSG and GNP using a laser with a wavelength of 532 nm.

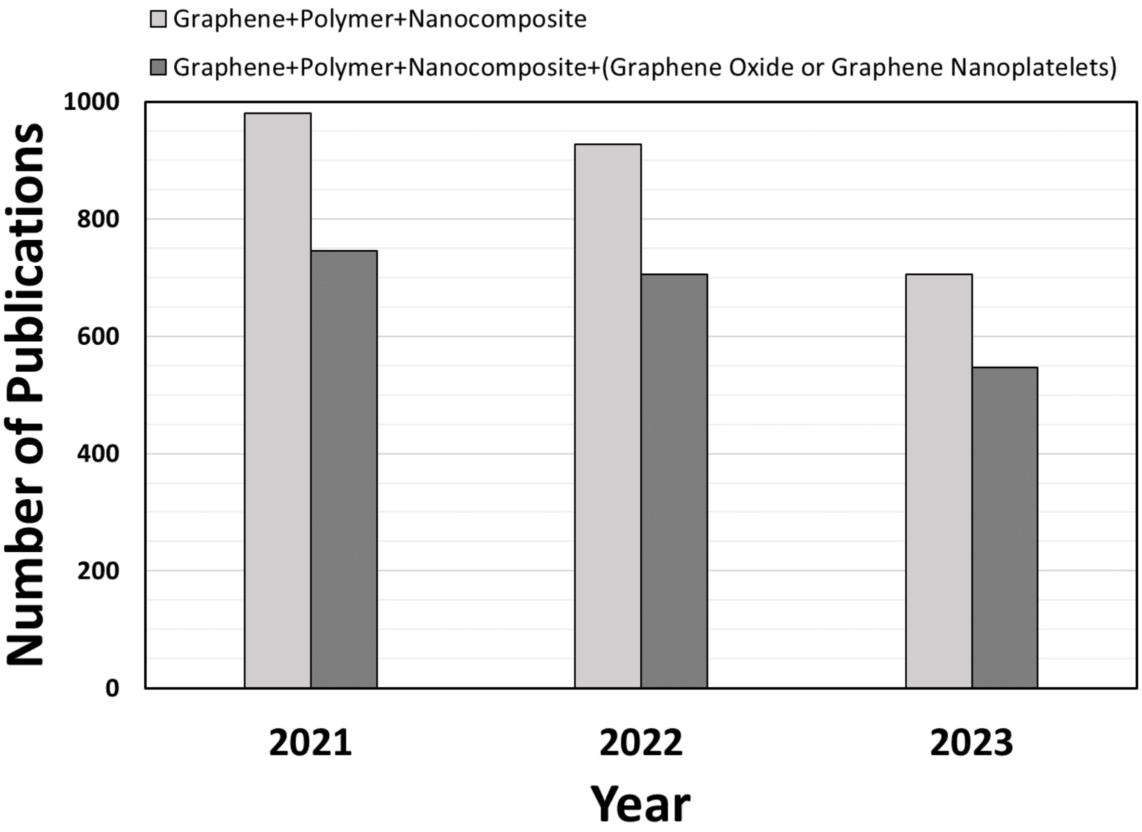

Figure S1. Bar graph showing the number of publications on graphene-filled polymer-matrix nanocomposites published in the years 2021, 2022, and 2023 (light gray bars). The number of publications on graphene-filled polymer-matrix nanocomposites containing either graphene oxide or graphene nanoplatelets is also shown (dark gray bars).

Figure S2. An injection molded ABS-matrix nanocomposite containing 0.1 wt% GSG.

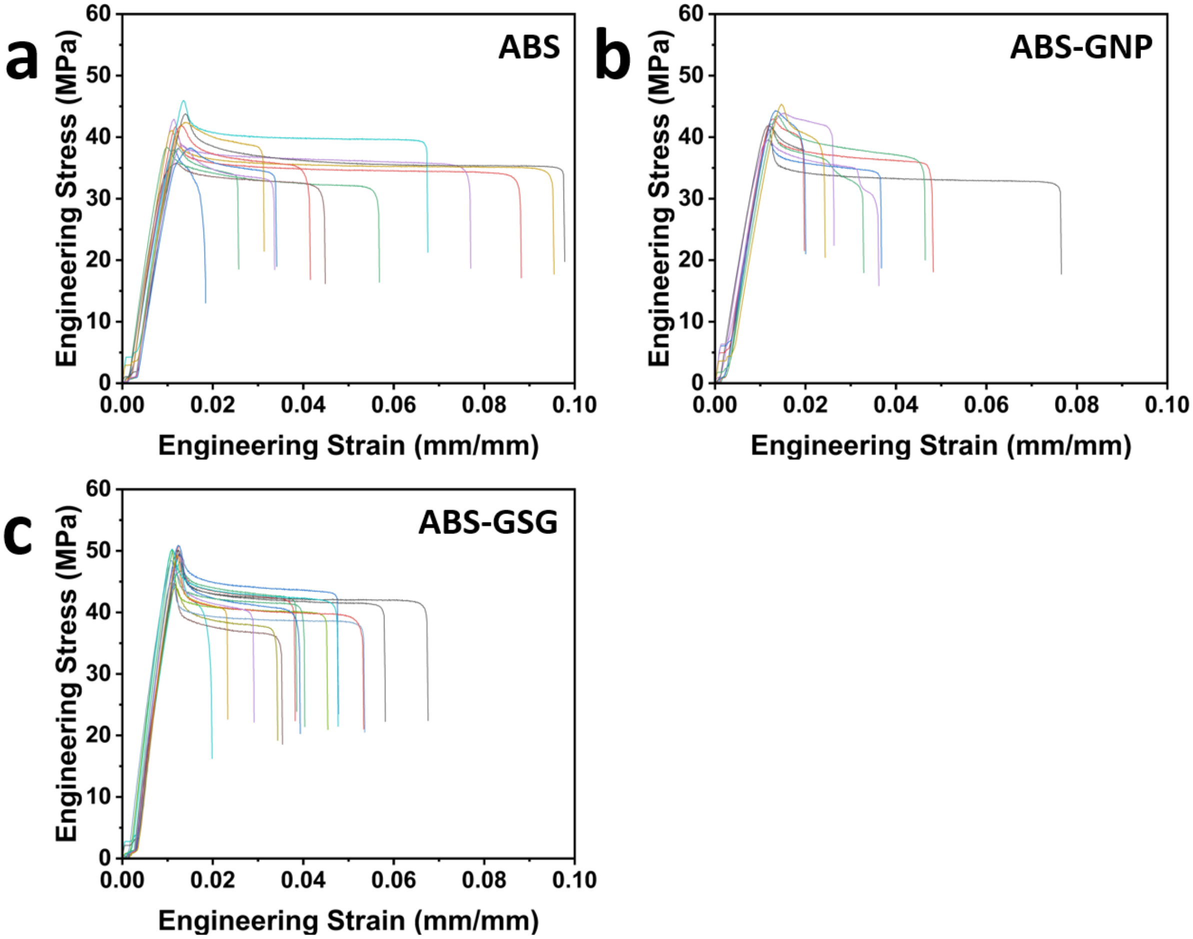

Figure S3. Engineering stress versus strain curves of (a) pure ABS, (b) ABS-GNP nanocomposites, and (c) ABS-GSG nanocomposites.