Multifunctional Polymer Nanocomposites Reinforced by 3D Continuous Ceramic Nanofillers

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* Supporting Information

ABSTRACT: Polymer nanocomposites with inclusion of ceramic nanofillers have relatively high yield strength, elastic moduli, and toughness that therefore are widely used as functional coating and films for optoelectronic applications. Although the mechanical properties are enhanced with increasing the fraction of nanofiller inclusion, there generally is an upper limit on the amount of nanofiller inclusion because the aggregation of the fillers in the polymer matrix, which typically occurs, degrades the mechanical and/or optical performances above 5 vol % of inclusions. Here, we demonstrate an unconventional polymer nanocomposite composed of a uniformly distributed three-dimensional (3D) continuous ceramic nanofillers, which allows for extremely high loading (~19 vol %) in the polymer matrix without any concern of aggregation and loss in transparency. The fabrication strategy involves conformal deposition of Al₂O₃ nanolayer with a precise control in thickness that ranges from 12 to 84 nm on a 3D nanostructured porous polymer matrix followed by filling the pores with the same type of polymer. The 3D continuous Al₂O₃ nanolayers embedded in the polymer matrix with extremely high filler rate of 19.17 vol % improve compressive strength by 142% compared to the pure epoxy without Al₂O₃ filler, and this value is in agreement with theoretically predicted strength through the rule of mixture. These 3D nanocomposites show superb transparency in the visible (>85% at 600 nm) and near-IR (>90% at 1 μm) regions and improved heat dissipation beyond that of conventional Al₂O₃ dispersed nanocomposites with similar filler loading of 15.11 vol % due to the existence of a continuous thermal conduction path through the oxide network.

KEYWORDS: nanocomposites, 3D continuous nanofiller, proximity field nanopatterning, atomic layer deposition, functional coating and films

Mechanically reinforced polymer nanocomposites are widely used as functional coatings and films for optoelectronic devices1,2 because of their low density (<2 g/cm³) and controllable mechanical properties including elastic moduli, strength, and toughness. A conventional strategy for reinforcement of polymeric materials is forming the polymer composites by dispersing relatively strong nanofillers such as ceramic nanoparticles3,4 two-dimensional (2D) flakes5–7 and carbon nanotubes (CNTs).8–10 Theoretically, the strengths and moduli of the polymer nanocomposites are known to be proportional to the volume ratio of dispersed nanofillers (referred to as the rule of
mixtures) when both phases are aligned in such a way to carry same amount of strains, but this optimal mechanical condition is usually hard to achieve due to aggregation and discontinuity of the nano fillers. For example, the epoxy composites containing 2.2 vol % SiO₂ nanoparticles report even lower strengths than the one with less particles (0.22 vol % SiO₂ nanoparticles), where the performance degradation is attributed to aggregation of the nanoparticles. Surface functionalization often helps improve the dispersion, but the maximum loading ratio even in this case appears to remain low only up to 5 vol %. Additionally, layered composites containing continuous interface between the constituent phases have been proposed to efficiently enhance the mechanical strength, but in this case the anisotropy in the layered structure limits favorable loading directions lying perpendicular to the stacking direction.

Construction of the cocontinuous composite materials composed of physically separated two-phase networks emerges as a promising methodology to overcome the aforementioned limitation on dispersibility of nanofillers in the matrix. In general, a two-step process is required to produce such cocontinuous composites: (1) preparation of open pore templates, followed by (2) infiltration of second phase fillers into the voids. While the commercial 3D printer would offer a convenient way to prepare the porous polymer templates, the spatial resolution of current technology renders the scales of fabricable features to remain relatively large, typically on the order of few hundred μm to mm. On the other hand, using 4-beam interference lithography Lee et al. have recently succeeded in scaling down the internal dimensions in epoxy/carbon cocontinuous composites with the periodic structures at the submicron scale. Although this lab-scale experimentation demonstrated the feasibility of superior mechanical performances, such as the specific energy absorption, of nanostructured polymer-inorganic composites, there is still no established fabrication technology to design and synthesize the nanostructured porous 3D polymer templates and cocontinuous composites at the macroscopically available scales. Greer et al. have not only demonstrated the significantly enhanced mechanical properties of the nanostructured porous materials but also comprehensively studied the mechanical effect of different microlattices for realization of ultrastrong and -light materials. In particular, the reported porous composites, which are fabricated by coating thin ceramic layer on the surface of the polymeric microstructures, exhibit effectively improved the mechanical strength. Additionally, X. Shen et al. demonstrated the enhanced thermal or electrical conductivity of cocontinuous composites composed of the interconnected and microstructured filler materials.

Here, we demonstrate an inch-by-inch scale production of nanostructured cocontinuous composite materials composed of the epoxy matrix reinforced by the 3D continuous ceramic nanolayers (thickness <100 nm). The fabrication processes sequentially consist of (i) proximity field nanopatterning (PnP), (ii) atomic layer deposition (ALD), and (iii) spin-casting infiltration, resulting in the production of the epoxy/Al₂O₃/epoxy 3D nanocomposites, in which the individual phases are fully interdigitated with each another (see Figure 1). The volume fraction of Al₂O₃ layer was determined by the deposition thickness (varying between 12 and 84 nm in this study). The resultant 3D nanocomposite shows greatly enhanced mechanical properties in both compressive strength (~142% enhancement at 19.17 vol %) and tensile strength (~53% enhancement at 9.32 vol %) compared to the monolithic solid epoxy. Additional functionalities such as transparency (>88% at 800 nm wavelength) and fast heat...
RESULTS AND DISCUSSION

A schematic illustration for the fabrication processes is presented in Figure 1a. Initially, 3D nanostructured porous epoxy template with the periodic body-centered tetragonal (BCT) symmetry is prepared to have the extrinsic area larger than 1 in. x inch using PnP technique. The dimensions of the BCT unit cell is ~600 nm x 600 nm x 1.9 μm (detailed geometric dimensions are given in Figure S1). Then, an amorphous Al₂O₃ nanolayer is conformally deposited on the surface of the epoxy ligaments using the ALD at the processing temperature of 90 °C (Figure S2a). The infiltration of the same epoxy with the preformed templates through the pores in the Al₂O₃ coated 3D nanostructures completes the synthesis of a solid nanocomposite containing three-continuous phases (epoxy/Al₂O₃/epoxy). The two epoxy parts are uniformly separated by Al₂O₃ nanolayers (Figure 1b–e). The porous 3D nanostructured epoxy template is optically opaque regardless of the existence of the Al₂O₃ nanolayer because of the light scattering on the air—matter interfaces (Figure S2b), but the samples become transparent after infiltration of same epoxy into the porous template due to the index-matching (Figure 1f). The effect of Al₂O₃ phase in the 3D nanocomposites on their optical behavior is almost negligible because the effective refractive index of the Al₂O₃ is relatively small considering its volume ratio (from 4.1 vol % to 19.17 vol %).

In order to understand the mechanical behavior of the 3D nanocomposites, the micron-scale uniaxial compression tests was conducted using in situ SEM nanoindenter (Hysitron PI-87) equipped with a flat punch diamond tip of 10 μm in diameter. In total, five sets of samples with different volume fractions of Al₂O₃ ranging from 0 (pure epoxy) to 19.17 vol % (Al₂O₃ thickness of 84 nm) (Figure 2a) were machined into micropillars with a diameter of 4 μm and a height of 12 μm using focused ion beam (FIB) milling. The movies capturing deformation behavior of the 3D nanocomposite micropillars are presented separately (Movies S1 and S2). The true stress vs strain curves were calculated assuming volume conservation during plastic deformation. The stress–strain responses shown in Figure 2b indicate that the strengths of the composites increase with the thickness or the volume fraction of Al₂O₃. The flow stress at 5% plastic strain of the sample with 19.17 vol % Al₂O₃ is 494.1 MPa, higher by 142% than the pure epoxy. In addition to the relative fractions, spatial distribution of each phase is also known to be an important factor to affect the mechanical behavior of the composite materials: the optimal performance occurs when they configure in such a way for the harder phase to carry as much load as possible, often known as equal-strain condition. When such condition is satisfied, the strength of composite materials becomes linearly dependent on the volume fraction of each phase (rule of mixture): σ = V_matrixσ_matrix + V_fillerσ_filler
where $V_{\text{matrix}}$ and $V_{\text{filler}}$ are the volume fractions of the matrix and filler, respectively, and $\sigma_{\text{matrix}}$ and $\sigma_{\text{filler}}$ are their strengths, respectively. Figure 2c (black squares) shows the compressive strengths of the 3D nanocomposites as a function of the volume fraction of the Al$_2$O$_3$ phase, together with the theoretically predicted values using the rule of mixture (strength of pure epoxy, 200 MPa, was directly measured on our specimen and that of Al$_2$O$_3$, 1.8 GPa, was found in the literature). It is noteworthy that the measured compressive strengths are almost identical with the theoretical prediction, implying that the configuration of the Al$_2$O$_3$ phases in our 3D nanocomposite ensures the equal-strain condition. It should also be noted that the measured compressive strengths are almost identical with the theoretical prediction, implying that the configuration of the Al$_2$O$_3$ phases in our 3D nanocomposite ensures the equal-strain condition. It should also be noted that the measured compressive strengths are almost identical with the theoretical prediction, implying that the configuration of the Al$_2$O$_3$ phases in our 3D nanocomposite ensures the equal-strain condition. It should also be noted that the measured compressive strengths are almost identical with the theoretical prediction, implying that the configuration of the Al$_2$O$_3$ phases in our 3D nanocomposite ensures the equal-strain condition.

Although the 3D BCT nanostructures used in our paper have relatively low symmetry, the solid 3D nanocomposites with the ceramic nanofiller embedded between polymer matrixes ensure much higher stability as structural materials than the porous 3D composites. This stability could be originated from the ductile-like deformation of the solid 3D nanocomposites unlike brittle failure of the porous materials. Additionally, carbon/epoxy nanocomposite has nearly the same value with the 3D nanocomposite reported in this work, assuming that the volume ratio of the fillers in both samples is equal to 50 vol %. However, due to technical limitation for fabricating large 3D nanostructures, the reinforcing effect of the 3D continuous nanofillers in cocontinuous 3D nanocomposites has not been proven on a practical-scale.

To further investigate mechanical responses of the 3D nanocomposites with BCT symmetry, we conducted finite element analysis (FEA) (see the Supporting Information for a detailed simulating method). The stress–strain curves obtained from the simulations are presented in Figure 2d. The 0.2% offset yield stresses are 242.92 MPa, 352.63 MPa, 445.61 MPa, and 503.82 MPa for the samples with 12 nm, 36 nm, 60 nm, and 84 nm Al$_2$O$_3$ thicknesses, respectively, which shows good agreements with our experimental results (within 5%). Figure 2e and Figure S4 shows the effective and von Mises stress at 5% uniaxial strain, and Figure S5 presents...
equivalent strain distribution at 5% uniaxial strain. Interestingly, both phases (epoxy matrix and Al2O3 layer) carry almost identical strain, and thereby the Al2O3 phase, which has higher elastic modulus than the epoxy, supports higher stresses than the matrix (Figure 2e and Figure S4): the situation close to the equal-strain condition ensures the linear dependency of strength on the volume fraction as well as the theoretical maximum strength that the composite materials can attain.

The in situ SEM mechanical characterization revealed that the monolithic epoxy micropillar deformed homogeneously throughout the entire compression, in which the strain in the micropillar distributes evenly along the axial direction of the pillar (Figure 2f and Figure S6). The ripples on the surface of the pillar after the compression test appear to stem from the viscous flow occurring in the epoxy. What is interesting, however, is that the sample with the highest yield strength (84 nm thick Al2O3 layer, 19.17 vol %) showed significant strain softening as plasticity proceeds, which contradicts our simulation results. Such strain softening behavior is also observed in 60 nm (15.11 vol %) micropillar but to a lesser extent. This softening behavior seems to be correlated with the occurrence of inhomogeneous deformation in the samples with high Al2O3 thickness (see Figure 2f). Plastic deformation starts at the top of the micropillar because the tapering effect, the inevitable artifact in the FIB milling, induces locally higher stress than at the bottom part. Once the top of the pillar has gone through plastic deformation, the morphology of the ceramic layers loses mechanical integrity and the materials become softer; thus, further plastic deformation is confined there. In other words, even when the volume fraction remains unchanged, load-carrying capability of 3D nanocomposites decreases with the breakage the ceramic phases, further confirming the importance of the structural continuity in the nanofillers.

To further demonstrate superior mechanical performances at a scale comparable to the whole specimens, the macroscopic tensile experiments are performed on the bulk 3D nanocomposites (Figure 3). The free-standing 3D nanocomposite films with 1 in.2 area are successfully delaminated from the substrate utilizing thin (~1 μm) water-soluble poly(acrylic acid) (PAA) sacrificial layers. The stress–strain curves show the intermediate plateau regions at strains between 0.006 and 0.015, which was not observed in the monolithic epoxy (Figure 3a). Such a plateau in the stress–strain curves is known to be caused by sequential breakage of constituent materials in layered nanocomposites. In our case, they are likely due to the fracture of the solid epoxy passivation layers between the substrate and the 3D nanocomposites, which were inevitably implanted during the fabrication process (detailed explanation can be found in the method section, Figures S7 and S8). The ultimate tensile strength (UTS) of the 3D nanocomposite linearly increases to 106.6 MPa with ceramic volume fraction until it reaches 9.32 vol %, which is 53% higher than that of the pure epoxy. However, unlike the compressive strengths, the UTS starts to decrease with further increase of nanofiller fractions. The possible reasons for this degradation occurring at large volume fractions could be found using the Weibull statistics, where the larger probability of flaw existence in the thicker nanofillers undermines their load-carrying capability. Especially, bulk-scale samples with thicker nanoshell (15.11 and 19.17 vol %) for measuring tensile strength have much higher probability of defect existence and therefore the degradation of UTS could be generated. Nevertheless, the 3D nanocomposites still show the significantly (40.3%) enhanced UTS at a high loading ratio of 9.32 vol % compared to the samples reinforced by the conventional nanoparticles (40 nm diameter) with equivalent volume fraction (Figure 3b). Again, this superiority should be attributed to continuous structures of nanofillers that can sustain stresses much more effectively than discrete, randomly distributed, or aggregated nanoparticles (Figure S9). Figure 3c shows the cross-sectional SEM images of the samples after tensile fracture. The monolithic epoxy film shows a very smooth fracture surface, while the 3D nanocomposites exhibit uneven and discontinuous morphologies. The degree of nonuniformity in the fractography of the 3D nanocomposites gradually increases as the volume ratio of the Al2O3 increases to 9.32 vol % and then becomes smooth again. This rough fracture surface is generally known as an evidence of the efficient load transfer between fillers and matrix materials, and therefore the continuous nanofillers (up to 9.32 vol %) in the 3D nanocomposites interact well with the epoxy matrix, which is consistent with the trend of UTS. Above optimal volume fraction (9.32 vol %), the nonefficient interaction may be due to an increased flaw ratio in the Al2O3 nanolayer and bulk-scale 3D nanocomposites. Figure 3d presents the relative enhancement of the UTSs and elastic moduli of our samples compared with other composite materials reported elsewhere. Although Al2O3 has a relatively lower intrinsic strength compared to other well-known high strength nanofillers such as carbon nanotubes (CNTs), boron nitrides (BN), or graphene (σ_{graphene}/σ_{Al2O3} ≈ 100), the excellent enhancement both in UTSs (~53%) and elastic moduli (135%) could be achieved by extremely high loading (~9.32 vol %) of continuous Al2O3 nanofillers. Figure 3e presents the FEA simulation results of the 3D nanocomposites under uniaxial tension, reporting tensile strengths of 82.4 and 120.48 MPa for 4.1 vol % and 9.32 vol % Al2O3 samples, respectively, showing good agreement (within 10%) with experimental measurements up to 9.32 vol %. Similarly to the compression cases, the continuity of each phase was confirmed again to play the significant role to amplify the mechanical performances under the tensile load as well (Figure 3f and Figures S10 and S11). However, in contrast to the experimental results, FEA results suggest incessant increase of strengths, possibly attributed to the nonexistence of flaws assumed during the simulation. To further analyze the effects of the rotational and/or reflective symmetries in the nanofiller geometry, i.e., the degree of isotropy, we performed additional computations to investigate the mechanical responses of nanocomposites in which the Al2O3 phases have the body centered cubic (BCC) and diamond structures (Figure S12). The dimensions of the diamond and BCC unit cell are ~600 nm × 600 nm × 600 nm and the degree of isotropy is much higher than BCT unit cell (600 nm × 600 nm × 1.9 μm). Figure 3g compares the simulated tensile stress–strain curves from 3D nanocomposites containing the same volume fraction of Al2O3 with different geometries: BCT, BCC, and diamond symmetry. Compared to the BCT sample, the diamond and BCC symmetry nanocomposites exhibit 21.23% and 20.28% enhanced tensile strength, respectively. This additional reinforcement is likely due to highly effective load carrying capability of the isotropic nanostructured fillers existed in both symmetries (Figure S13).

The 3D nanocomposites with 3D continuous Al2O3 nanolayers not only show improved mechanical strengths but also show excellent optical, thermal, and flexible properties.
Figure 4 a shows the transmittance spectra of the 3D nanocomposites with different volume fractions (4.1, 9.32, 15.11, and 19.17 vol %) of Al2O3 nanolayers in the visible and near-IR regions from 400 nm to 1 μm, compared to the reference (pure epoxy; indicated as a black line). The total thickness of the samples for measuring the transmittance is equal to 11 μm. The numerous light scattering from the porous structure of the initial template can be removed by infiltrating these epoxy into the template to create a solid nanocomposite. After the second epoxy occupies the interstitial air portion inside, the transmittance of the 3D nanocomposite (4.1 vol % Al2O3) recovers from ∼0.24% to ∼87% at the wavelength of 600 nm due to the index-matching effect. (Figure 4a and Figure S2c) However, the transmittance of the 3D nanocomposite is still about 6% lower than that of pure epoxy (∼93%), which results from the refractive index of the embedded Al2O3 nanolayer (nAl2O3 ∼ 1.58) being slightly different from that of the epoxy matrix (nepoxy ∼ 1.66). As the volume fraction of Al2O3 nanolayer in the 3D nanocomposites increases, the transmittance drops slightly further which is still much better than that of the nanoparticle-based conventional nanocomposites with similar volume fractions.33 Additionally, the 3D continuous Al2O3 nanolayers offers an effective thermal conduction path in the nanocomposite, resulting in faster heating and cooling rates than both pure epoxy and the epoxy nanocomposite reinforced by Al2O3 nanoparticles with identical volume fraction (15.11 vol %). One end of the rectangular cut samples are fixed on a hot plate and are heated at the same time, and the temperature distributions of the samples after 10 s are visualized by an IR camera (Figure 4b and Figure S14a). Plotting the temperature gradient along the distance from the heating zone shows that the 3D nanocomposite film delivers heat faster than the pure epoxy and conventional epoxy nanocomposites (nanoparticle dispersed epoxy) films (Figure 4c and Figure S14b). After reaching the saturated temperature (60.8 °C), the samples begin to cool simultaneously in the atmosphere. After 10 s, the temperature of the 3D nanocomposite film is lowered dramatically to 33.9 °C, while the temperature of the pure epoxy films is still above 40 °C. In addition to superior optical and thermal properties, the 3D nanocomposites are mechanically strong, but flexible, because their total thickness is only ∼11 μm (Figure 4d). The 3D nanocomposite behaves reversibly within a certain degree of bending range (roughly within radius of curvature of 3 mm, when the volume fraction of the Al2O3 nanolayer is 15.11 vol %). The 3D nanocomposite film developed here can be simply transferred to optoelectronic devices such as photovoltaics and displays, as we demonstrate by attaching it on a smart watch and a smart phone and can play a useful role as multifunctional coatings and films for optoelectronic devices (Figure 4e,f).
CONCLUSION

In summary, we have developed an unconventional 3D nanocomposite that contains a continuous network of inorganic reinforcing materials that could sustain the strengthening effect at extremely high loading ratio of filler, unlike the conventional nanoparticle-dispersed nanocomposites. The filler loading is precisely controllable, up to ~19.17 vol % Al2O3 and the 3D nanocomposites showed highly enhanced compressive strength of 494.1 MPa, which is a 142% enhancement over the pure epoxy. Through theoretical calculation and FEA simulation, we demonstrate that the 3D nanocomposites have near theoretical strength. Similar trends were also shown in tensile test of bulk scale specimens. In addition, the films showed fast heating and heat dissipation resulting from a 3D continuous heat conduction path throughout the nanocomposite while also having superior transparency and flexibility. Bulk scale production of such 3D nanocomposites represents a promising future use of the process and materials developed here and exploring other type of nanofillers with useful material properties such as ultrahigh strength (e.g., graphene and BN) or electrical conductivity (e.g., ZnO and TiN) will be an interesting future study.

EXPERIMENTAL SECTION

Preparation of Photoresist-Coated Substrates. As a sacrificial layer, a poly(acrylic acid) (PAA, 10 wt % dissolved in water) was spin-coated at 3000 rpm with ~1 μm thickness on the cleaned glass substrate and then baked at 190 °C for 2 min for evaporation of water solvent. To prevent swelling of PAA by water vapor during developing, a fully exposed and hard-baked passivation layer (SU-8, ~1 μm) was first coated on the PAA layer. The photoresist film with a 10 μm thickness was then spin-coated on the passivation layer at 2000 rpm for 30 s. The resist-coated substrate was subsequently soft-baked at 95 °C for 10 min.

Fabrication of 3D Nanocomposites. A 3D nanostructured epoxy was prepared through PnP techniques composed of several optical components and phase mask. We reported the fabrication method of the phase mask and detailed procedure of PnP technique in previous papers.26 Al2O3 was deposited on the surface of the 3D epoxy by atomic layer deposition (ALD, Scientech) at low temperatures (90 °C). Trimethyl aluminum (TMA, UP chemical) was prepared using an Al2O3 precursor and H2O as a reactant. Epoxy resin (SU-8) was spin coated on the Al2O3 coated samples at 6000 rpm for 30 s to fabricate the 3D nanocomposites. The epoxy infiltrated samples were baked at 95 °C for 30 min and exposed under UV lamp (1 mW/cm²). After post bake at 95 °C for 30 min and hard bake at 190 °C for 5 min to enhance interfacial bonding between the epoxy and Al2O3, finally the 3D nanocomposites are prepared. Amorphous Al2O3 nanoparticles (US Research Nanomaterials) are functionalized by 3-Glycidoxypropylmethoxysilane (GPS, Sigma-Aldrich) and then the epoxy functionalized nanoparticle were mixed in epoxy resin (SU-8). Finally, the conventional nanocomposites containing Al2O3 nanoparticles were attained by spin coating the composites on the substrate. The top surfaces of the samples are partially etched using a reactive ion etcher (RIE) to remove the overcoated residual epoxy (Figure S3).

Nanopillar Compression Test. A Quanta 3D FEG FIB was utilized to fabricate nanopillars with diameters of 4 μm and heights from 10–12 μm (aspect ratio L/D ~ 3) for epoxy resin and 3D nanocomposites with 12, 24, 36, 60, and 84 nm thickness of Al2O3 nanofiller. The nanopillar compression testing was performed using a Hysitron picoindentation system (PI-87) fitted with a flat punch tip (10 μm) at a nominal constant displacement rate of 10 nm s⁻¹, which translates to an engineering strain rate of 0.001 s⁻¹.

Tensile Test. A self-standing films of the 3D nanocomposites were prepared by removing PAA layer for 24 h in a water. The tensile mechanical properties were measured using an Instron 8845 Microforce tester (50 N). The tests were conducted at a load speed of 0.2 mm/min. The specimens were obtained by cutting down from the self-standing 3D c-epoxy films with length of 25 mm and width of 5 mm. The results of mechanical test listed in the paper are the average values of at least five tests.

Other Characterizations. The surfaces and cross sections of the samples were observed using a field emission scanning electron microscope (FESEM, S-4800, Hitachi). Elemental mapping was measured by energy dispersive spectroscopy (EDS, Magellan 400, FEI). The phase of the samples was identified using an X-ray diffractometer (XRD, D/MAX-2500, Rigaku) with Cu Kα radiation. UV–vis spectroscopy (UV-310PC, Shimadzu) was used for measuring the transmittance of the samples. The infrared thermal image was identified using an infrared thermo-graphic camera (FLIR T400, FLIR company). The refractive index of the samples was measured with an ellipsometer (ALPHA-SE, J.A. Woollam).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b03264. Detailed method regarding simulation and calculation of the mechanical properties and additional simulation and experimental data (PDF) Compression test of pure epoxy (AVI) Compression test of 3D nanocomposites (AVI)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Samsung Research Funding Center of Samsung Electronics under Project Number SRFCA1501-02. This research was supported by Multi-Ministry Collaborative R&D Program (Development of Techniques for Identification and Analysis of Gas Molecules to Protect Against Toxic Substances) through the National Research Foundation of Korea (NRF) funded by KNPA, MSIT, MOTIE, ME, NFA (Grant 2017M3D9A1073501). This work was supported by National Research Foundation (NRF) of the Korea government (MSIP) under Grant 2016R1A2B3011473.

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