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Bio inspired Magnet-polymer (Magpol) Actuators

Anansa S. Ahmed and R.V. Ramanujan

School of Materials science and Engineering, Nanyang Technological University,

Singapore 639798

ABSTRACT

Magnet filler–polymer matrix composites (Magpol) are an emerging class of morphing materials. Magpol composites have an interesting ability to undergo large strains in response to an external magnetic field. The potential to develop Magpol as large strain actuators is due to the ability to incorporate large particle loading into the composite and also due to the increased interaction area at the interface of the nanoparticles and the composite. Mn-Zn ferrite fillers with different saturation magnetizations (Ms) were synthesized. Magpol composites consisting of magnetic ferrite filler particles in an Poly ethylene vinyl acetate (EVA) matrix were prepared. The deformation characteristics of the actuator were determined. The morphing ability of the Magpol composite was studied under different magnetic fields and also with different filler loadings. All films exhibited large strain under the applied magnetic field. The maximum strain of the composite showed an exponential dependence on the Ms. The work output of Magpol was also calculated using the work loop method. Work densities of upto 1 kJ/m^3 were obtained which can be compared to polypyrrole actuators, but with almost double the typical strain. Applications of Magpol can include artificial muscles, drug delivery, adaptive optics and self healing structures. Advantages of Magpol include remote contactless actuation, high actuation strain and strain rate and quick response.

Keywords: Magnet polymer composites, actuators, work loop, multifunctional, morphing

1. INTRODUCTION

Living organisms are able to sense and interact with their environment through movement or change in shape or structure on both macro and micro scale. Thus research in bio inspired shape changing materials and structures have attracted intense interest due to their attractive ability to morph and adapt to environmental conditions.[1-2] Current actuation technologies are based either on high modulus – low strain materials, such as piezoceramics and magnetostrictors, or on multi-component systems, such as hydraulic, pneumatic or electromagnetic devices.[3] The former technologies are capable of working at high stresses but low strains, whereas the latter systems are capable of producing large strains or displacements but at comparatively low stresses. Considerable attention has also been directed at shape memory alloys (SMAs) that can deliver both high forces and large displacements. However, the response times and longevity of these materials has yet to be optimized to afford reliable actuator technologies.[4] It is clear from an analysis of the performance indices of mechanical actuators that there is a gap between the high stress-low strain and the low-stress – high strain groups.[4] This is the region where most current systems like EAPs and MagPol operate. The remote activation, high strain rate and quick response of Magpol make it an attractive alternative as an actuating material.[5-6]

Magnet filler–polymer matrix composites (Magpol) are a class of materials that can be adapted to develop multifunctional composites;[7] Other materials similar to Magpol are ferrogels, magnetorheological elastomers and magnetoactive polymers.[8-11] The advantage of Magpol lies in the flexible choice of matrix materials, for example hydrogels, silicone, polyurethanes and rubber have been used as matrices for the development of Magpol; A corresponding flexibility exists in the choice of magnetic filler. The filler material can be magnetically soft or hard. [12-13] Magpol has several advantages due to its unique composition and flexibility in choice of polymer and filler. The materials used in the synthesis of Magpol impart it with the ability for remote contactless actuation, actuation in various modes, high actuation strain, self-sensing and quick response. The ability of the composite to actuate in a magnetic field as well as to generate heat in an AC field makes this an ideal system to study multifunctionality.

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The use of Magpol as actuators has been studied by various groups. It was determined that magnet polymer composites can be deformed by both uniform and non uniform magnetic fields.[14] In a nonuniform magnetic field, forces act on the magnetic particles due to the magnetic gradient. Due to the magnetic interaction between the magnetic particles and the interactions between the particles and the polymer chains, changes in molecular conformation accumulate and eventually lead to shape changes. The final shape is established by the balance between magnetic forces acting on the particles and the elastic resistance of the polymer matrix. Different modes of shape change have been observed in Magpol materials including deflection, bending, elongation, contraction, or a combination of the above.[15-16]

This study reports the synthesis and characterization of $MnZnFe_2O_4$/thermoplastic polyethylene vinyl acetate (EVA) nanocomposites capable of large deformation under applied magnetic fields. The dependence of actuation on the saturation magnetization of the filler as well as the loading of the filler was also studied. This paper also describes the work loop measurements conducted on Magpol films during deflection type of deformation.[6] This scheme can potentially be extended to different magnetic fillers and polymer matrices with suitable choice of chemistry and optimization of properties.[17]

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials

All materials were used as received without further purification. manganese(II) chloride tetrahydrate 99%($MnCl_2$. $4H_2O$), zinc chloride, anhydrous (98+%) ($ZnCl_2$), iron (III) chloride hexahydrate, ($FeCl_3$. $6H_2O$), sodium hydroxide (NaOH) were purchased from Alfa Aesar. Poly(ethylene-co-acrylic acid) 15wt% and 1,1,2,2 tetrachloroethane were obtained from Sigma Aldrich. Polyethylene vinyl acetate brand Cosmothene EVA KA-31 (28% VA content) was purchased from the Polyolefin Company (Singapore) Pvt. Ltd. MilliQ water was used for all experiments.

2.2 Sample Preparation

Synthesis of the nanoparticle was done *via* the hydrothermal method. Manganese ($MnCl_2$), zinc ($ZnCl_2$) and iron chloride salts ($FeCl_3$) were dissolved in appropriate molar quantities in MilliQ water. The salt solutions were then added together and vigorously stirred while adding sodium hydroxide until the reaction mixture reached a pH of 12. The solution was placed into a hydrothermal vessel and heated in an oven for 4 hours at 190°C. The particles were then washed with DI water and ethanol and used for further experiments. 2sets of nanoparticles were synthesized with different Ms values by changing the Mn to Zn ratio. $Mn_{0.7}Zn_{0.3}Fe_2O_4$ and $Mn_{0.8}Zn_{0.2}Fe_2O_4$ compositions were synthesized and will be referred to as Mn0.7 and Mn0.8 respectively.

EVA-magnetic nanoparticle composites were synthesized by the solution casting method. EVA pellets were dissolved in 1,1,2,2 tetrachloroethane (TCE) on a hot plate at ~120°C. Nanoparticles were then added to the solution at the desired loading and the solution was immediately poured into petri dishes and heated at 120°C for 4 hours in an oven. Films were made with nanoparticle loadings of 10 wt%, 12 wt. % and 16 wt% and were ~150 μm thick.

2.3 Characterization

The crystal structure of the Mn-Zn ferrites were studied using a Shimadzu 6000 X-ray Diffractometer (XRD) with CuKα radiation of wavelength 1.54056 Å, in the 2θ range of 20°–80° at a scan rate of 2° min^{-1}. Phase identification was performed by matching peak positions and relative intensities to reference JCPDS files. The crystallite size was calculated using the Scherrer formula. The magnetic properties of the materials were determined using a Lakeshore 7404 Vibrating Sample Magnetometer (VSM) in an applied field range of 0–10 kOe. The mechanical properties of the polymer were also studied using the Physica MCR501 rheometer.

2.4 Displacement and Work Loop Measurements

The magnetic field used for all actuation measurements was produced by a Lakeshore CM-4 dipolar electromagnet with an air gap of 2.5 cm. The end of the sample was secured to an aluminum clamp and attached to an aluminum supporting stand, while the other end was strapped by a thread. Thereafter, the thread on the end of the sample was connected to the force gauge. The sample displacement was measured using an Acuity AR600 triangulation laser displacement sensor and the generated force was recorded using a Vernier dual range force sensor.

The Work-Loop technique, usually used in biological applications, was used in the project to measure the amount of work Magpol composites can produce. The sample was stretched up to a certain value of strain, which was ±50% in this case, while force was measured at every 0.5 cm of elongation. Thereafter, at 50% elongation, the sample was subjected to a magnetic field, and the maximum force was measured again at the maximum magnetic field. While in the presence of maximum magnetic field, the sample was then released slowly while the decrease of the force for various lengths after being released was recorded. The change of force for various levels of strain would form a loop; the area will give the work the magnet-polymer composite can produce.

3. RESULTS AND DISCUSSION

3.1 XRD

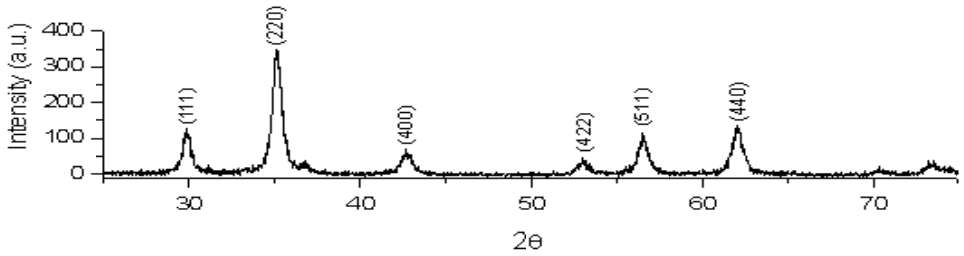

Figure 1: XRD pattern of Mn0.8 nanoparticles with peaks matching JCPDS card No. 10-0467

The XRD pattern shows that the synthesized nanoparticles have characteristic peaks of cubic spinel structure as seen in Figure 1. Peaks are observed at 29.9°, 35.2°, 42.6°, 52.9°, 56.3°,and 61.9° which match the franklinite spinel structure (JCPDS card No. 10-0467). The Scherrer equation was used to calculate the of the average crystallite diameter. The average size of the nanoparticles is 13 nm for both sets of particles.

3.2 Magnetic Properties

The room temperature hysteresis curves of the magnetic nanoparticles are shown in Figure 2. The saturation magnetization of the Mn0.8 nanoparticles was 66 emu/g, while the Mn0.7 nanoparticles only reached a maximum Ms of 50 emu/g. VSM measurements yield a anhysteric magnetization curve for the nanoparticle samples, indicating the formation of superparamagnetic nanoparticles.

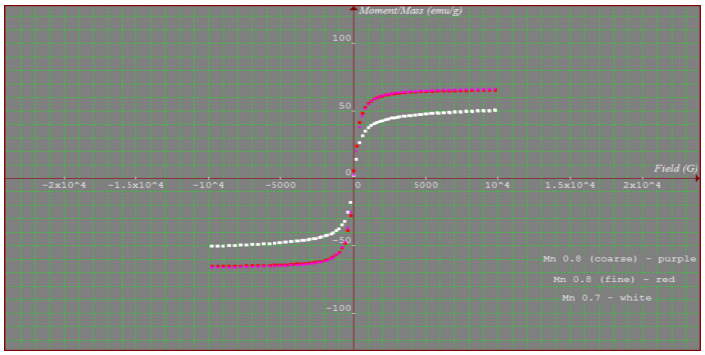

Figure 2: VSM data for the as synthesized $Mn_xZn_{1-x}Fe_2O_4$ magnetic nanoparticles

The magnetic properties of the films with wt% loadings of 2, 5, 10, 20, 40 and 60 % were also measured for both the Mn0.7 amd Mn0.8 samples (Figure 3). From Mn0.7 - 2% to 60%, the coercivity drops from 51.461 G to 17.903 G while the saturation magnetization increases from 2 emu/g to 15.2 emu/g. Likewise in the case of Mn0.8 - 2% to 60%, the coercivity drops from 55.8 G to 45 G while the saturation magnetization increases from 2.1 emu/g to 21.2 emu/g

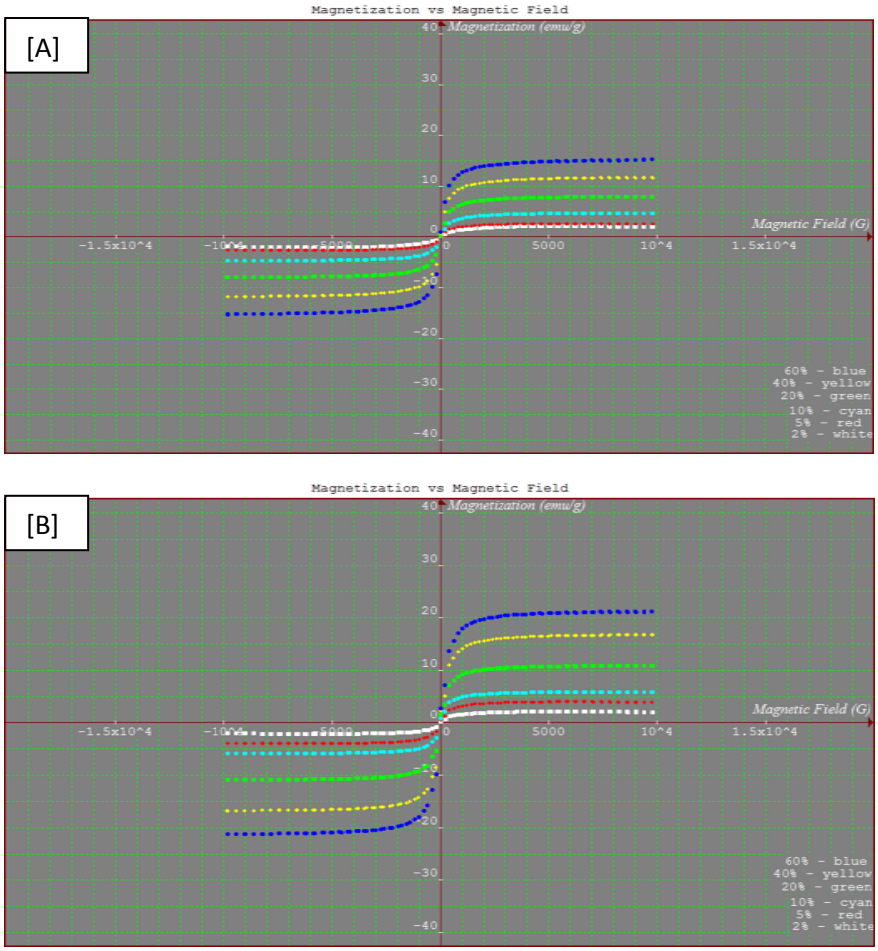

Figure 3 VSM data for the Magpol films containing different wt% loading of A] Mn0.7 and B] Mn0.8 nanoparticles

3.3 Mechanical Characterization

The rheological measurements showed that the storage modulus of the composite was consistently lower than that of pure EVA for all the samples. No clear trend was observed in the storage modulus (G') with increasing loading. G' values for the Magpol composite lay between 10 MPa an 25 MPa, while the EVA polymer without filler had a G' value of 32 MPa

3.4 Magnetomechanical Characterization

It is well known that magnetic materials can change their shape due to magnetic forces acting on their body, the study of this phenomenon is called magneto-solid mechanics. However, the unique properties of the large deflection and the threshold in deflection can only be found in Magpol because of its unique combination of magnetic properties and high flexibility. The "soft" mechanical properties play a crucial role in the magneto - elasticity observed in Magpol. The different threshold values at different particle concentrations can lead to interesting can be useful for switching applications. Figure 4 shows the displacement in different wt% loaded

samples by varying the magnetic field. Low loading samples show threshold behaviour, while the saturation magnetization of the samples influences the strain rate.

The threshold deflection behaviour can be explained by the nature of the magnetic field and magnetic field gradient produced by the electromagnet. Magnetic field measurements show that beyond a certain distance from the electromagnet, both the field and gradient are negligible. Both these quantities increase as the distance from the point of measurement to the magnet decreases, though the gradient changes at a much faster rate than the magnetic field strength. This drastic change in gradient accounts for the threshold behavior of the deflection of Magpol.

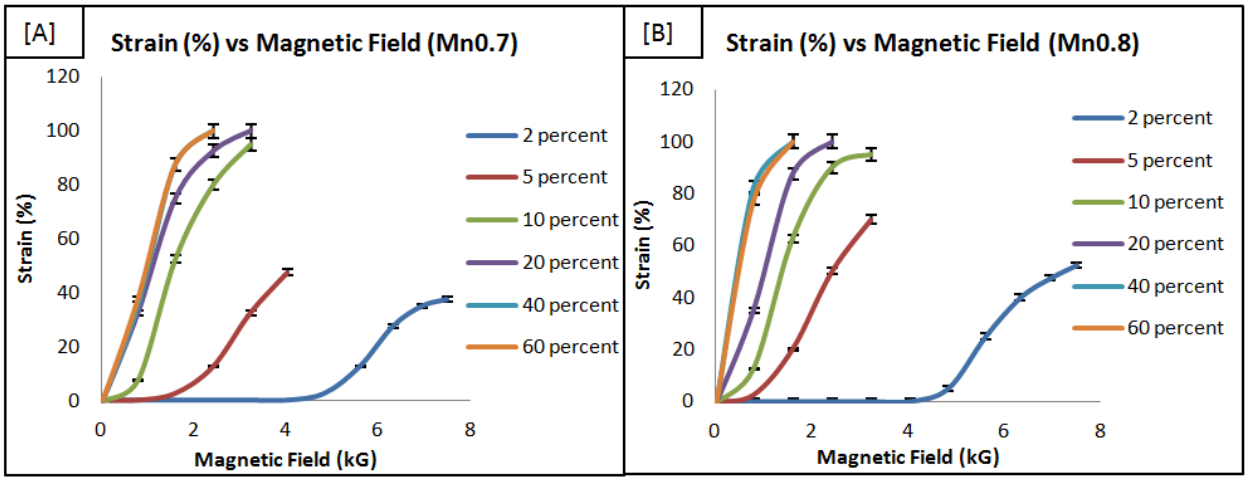

Figure 4 Magpol film displacement plotted against magnetic field for A] Mn0.7 filler and B] Mn0.8 filler with varying wt% loading

The deflection behaviour of Magpol depends on the force acting on the volume of the material (V) and is proportional to the magnetic potential U. The force (F) can be calculated from the magnetic moment (M) and the field gradient. The magnetic moment in turn depends on the applied field (H_0) and the susceptibility of the samples (χ).[17]

$$\frac{d\vec{M}}{d\vec{H}} = \chi \tag{1}$$

$$\vec{U} = \int_0^H \vec{M} d\vec{H} \tag{2}$$

$$\vec{U} = \frac{1}{2}\chi H_0 \tag{3}$$

$$\vec{F} = -\vec{\nabla}\vec{U} \tag{4}$$

$$F_y = M_y \int_0^V \frac{dH_y}{dy} dV \tag{5}$$

As the field is increased the film gradually moves towards the magnet, eventually the film reaches a point where the magnetic force is greater than the weight of the film and this results in maximum deformation. As the equations suggest, higher loading samples have greater susceptibility and thus show displacement even at low fields. In the case of the Mn0.7 and Mn0.8 samples, the same loadings have different susceptibilities. Thus, Mn0.8 samples show higher displacement at lower fields and higher strain rates. However when the applied field and therefore the force becomes greater than that required for complete deformation, the maximum deflection for both Mn0.7 and Mn0.8 samples is the same. (Figure 5)

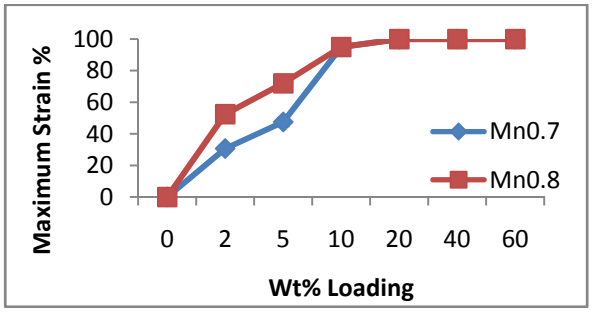

Figure 5 Maximum strain vs. nanoparticle loading

3.5 Work Loop

In addition to morphing ability, the actuation properties of MagPol were also studied in relation to work. The ability of Magpol to perform work was studied using the work loop method employed in artificial muscles studies. The work loop measurements are useful in designing sample dimensions, load, filler concentration etc. for Magpol based actuating devices. Figure 6 shows the work loops obtained for 20wt%, 40 wt% and 60 wt% samples of the Mn0.7 and Mn0.8.

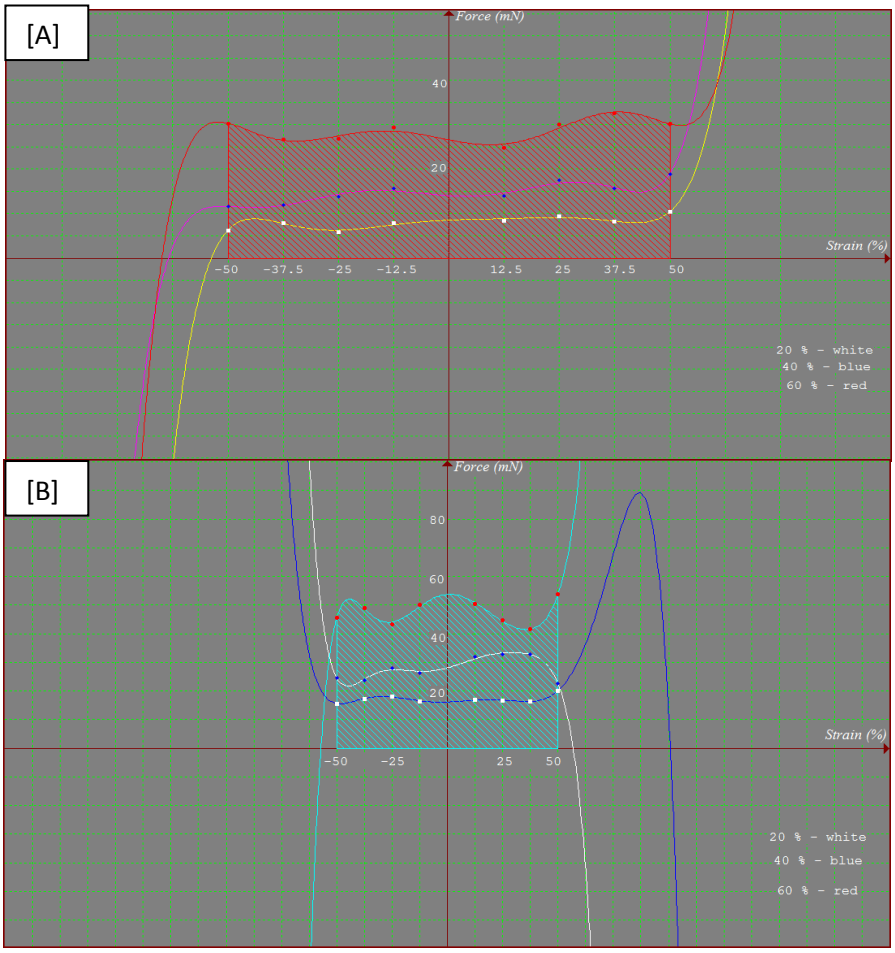

Figure 6 Work loops for Magpol films containing A] Mn0.7 and B] Mn0.8 fillers with 20, 40 and 60 wt% loading

Table 1 shows the maximum work output and stress generated by the composite. Increasing the loading results in larger force being generated. Unlike the strain, which shows saturation after a particular loading and applied magnetic field, no saturation behaviour is observed in the work output. Higher saturation magnetization results in higher stress and greater work output.

Table 1: Maximum Stress and work output obtained from Magpol composites through work loop method

Loading wt%	Mn0.7		Mn0.8	
	Max. Stress (Pa)	Work (μNm)	Max. Stress (Pa)	Work (μNm)
20	34.62	324	66.8	675
40	63.1	582	109.5	1139
60	108.5	1135	167.7	1913

While much larger stress and work output values have been obtained for other types of Magpol actuators using different fillers and matrix,[6] the components of this particular composite have additional advantages in the development of a multifunctional composite. Further work is necessary to optimize the parameters needed to obtain the highest output.

4. CONCLUSIONS

We have presented a bioinspired composite capable of actuation using a magnet-polymer based system.

- We synthesized magnetic $Mn_xZn_{1-x}Fe_2O_4$ nanoparticles with varying saturation magnetization using the hydrothermal method
- The ferrite nanoparticles were then used as a filler in an EVA matrix to make Magpol films with different filler loadings and therefore different Ms values.
- The ability of the composite to actuate under an external applied magnetic field was demonstrated. Higher deformation was observed for larger loadings but reached a saturation value at 20 wt%. It was observed that the morphing ability and strain rate of Magpol depended on the saturation magnetization of the nanoparticle filler.
- The Work loop method was used to study the work output. As no saturation behaviour was observed in the magnetic field range used in this investigation, it can be concluded that larger applied fields will result in greater work output. Though large strains were obtained for the Magpol films, work output was relatively low.

The advantage of this new class of actuator is the lack of a requirement for an integrated driving source. This may lead to a wide range of applications which require contactless, noninvasive control, such as human implants and aerospace devices[7, 18-19]. Thus Magpol is a promising new material which is ideally suited to the development of multifunctional smart structures.

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