# Magnetically Directed Co-nanoinitiators for Cross-Linking Adhesives and Enhancing Mechanical Properties

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eco-friendly approach and a wide range of potential in both science and engineering. However, the conventional means for the initiation of polymerization cannot define the desirable location of polymerization, which is often exacerbated by the poor temporal control in the curing system. Herein, the copper-immobilized dendrimer-based magnetic iron oxide silica (MNPs-G2@Cu<sup>2+</sup>) conanoinitiators are rationally designed as initiators for redox radical



polymerization. The nanoinitiators are magnetically responsive and therefore enable localized polymerization using an external magnetic field. In this work, anaerobic polymerization of an adhesive composed of triethylene glycol dimethacrylate, tert-butyl peroxybenzoate, and MNPs-G2@Cu<sup>2+</sup> as the magnetic co-nanoinitiators has been investigated. The use of a magnet locates and promotes redox free radical polymerization through the synergistic functions between peroxide and MNPs-G2@Cu<sup>2+</sup> conanoinitiators. The mechanical properties of the resulting polymer are considerably reinforced because the MNPs- $G2@Cu^{2+}$  conanoinitiators concurrently play another crucial role as nanofillers. This strategy provides a novel approach for magnetically tunable localized polymerization, which allows new opportunities to govern the formulation of advanced adhesives through polymerization under hazard-free conditions for various promising applications.

KEYWORDS: triethylene glycol dimethacrylate, TRIEGMA, anaerobic adhesive, localized polymerization, magnetic nanoinitiator, magnetic dendrimer

## INTRODUCTION

Many air-sensitive reactions or manufacturing processes of polymers intrinsically require a deoxygenated/anaerobic atmosphere to avoid interactions with a reactive or unstable form of oxygen, which produces undesirable byproducts. Anaerobic adhesives<sup>1</sup> are typical examples that are purposely designed for use under low-oxygen or deoxygenated conditions that can be found in the sophisticated, complex, and tight space or surface irregularity. Therefore, anaerobic adhesives are used in locking, sealing, retaining, and bonding applications, which are crucial in the electronics,<sup>2,3</sup> packaging,<sup>4</sup> and automobile industries.<sup>3</sup> Moreover, anaerobic adhesives stand out in certain aspects, such as accessibility, storage longevity, and eco-friendliness compared to other types of adhesives. Anaerobic adhesives are one-component and solvent-free adhesives that consist of dimethacrylate monomers. The cross-linking occurs in the absence of oxygen based on radical polymerization. For example, the redox radical initiation of anaerobic adhesive polymerization can be tailored by the decomposition of peroxide species at

room temperature caused by the presence of appropriate transition metal ions in the polymerization system.<sup>6</sup> However, conventional activation approaches, such as thermal, chemical, photochemical, redox, and mechanical means, can only initiate the polymerization but have limited control of the polymerization over the desirable area during the curing process.

To overcome the challenge of localized polymerization or adhesive formation, a magnetic field responsive approach has been chosen to realize magnetically controllable localized polymerization because an external magnetic field has various advantages such as being spontaneous, safe, effective, eco-

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Scheme 1. Overview of (a) Anaerobic Adhesive Polymerization and (b) Magnetic Dendrimer Co-nanoinitiators (MNPs-G2@Cu<sup>2+</sup>)



friendly, and untethered. Therefore, magnetic nanoparticles (MNPs) are appropriate solid support materials for use as magnetically responsive nanocarriers. Their unique and robust physicochemical properties,<sup>7</sup> such as intriguing chemical, magnetic, electrical, and optical properties, including a large surface area and biocompatibility, allow magnetic nanoparticles to be used in a broad spectrum of applications, especially in the fields of nanoscience and nanotechnology,<sup>8,9</sup> for instance, magnetic storage devices,<sup>10</sup> biomedical engineering,<sup>11</sup> environmental science,<sup>12</sup> and biotechnology.<sup>13</sup>

The surface properties of the magnetic particles can be tuned by using appropriate functional linkers and/or compounds to achieve remarkable advanced nanostructures. A dendrimer is a well-defined and highly branched macromolecule, which is constructed in an orderly manner with building blocks or branching units to form a generation (G).<sup>14</sup> The size (generation) corresponds to the density of functional groups on the dendrimer.<sup>15</sup> In particular, the triazine dendrimer exhibits promising properties such as molecular recognition and selfassembly through the acceptance and donation of hydrogen bonds,  $\pi - \pi$  interaction, and metal chelation.<sup>16–18</sup> Apart from the advantages mentioned above, the treelike structure of the dendrimer can firmly form dendrimer-coordinated transition metal complexes,<sup>19</sup> which can be employed as the redox sites during the chemical reaction.

It is notable that inorganic materials, such as inorganic nanoclay,<sup>20</sup> graphene oxide,<sup>21</sup> MXene,<sup>22</sup> carbon nanomateri-als,<sup>23</sup> layered double hydroxide,<sup>24</sup> and silica nanoparticles,<sup>25</sup> have also been used as nanofillers<sup>26–29</sup> to improve the intrinsic mechanical properties of polymers. The physical and chemical interactions between inorganic nanofillers and polymer chains allow the formation of stronger bonds.<sup>30,31</sup> Herein, the desirable copper-immobilized dendrimer will be integrated on core-shell magnetic iron oxide-silica nanostructures, namely core-shell MNPs-G2@Cu<sup>2+</sup>, as co-nanoinitiators and nanofillers for redox radical polymerization of anaerobic adhesives, which are responsive under external magnetic field control. The polymerization was carried out by using the anaerobic adhesive monomer [triethylene glycol dimethacrylate (TRIEGMA)], tert-butyl peroxybenzoate, and the judiciously designed copperimmobilized dendrimer-based magnetic iron oxide-silica (MNPs-G2@Cu<sup>2+</sup>) co-nanoinitiators as shown in Scheme 1a. This strategy provides an unprecedented approach for magnetically triggered localized polymerization that results in the

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**Figure 1.** Characterization of magnetic nanoparticles (MNPs). TEM images of (a) MNPs and (b) core-shell MNPs@SiO<sub>2</sub> NPs. (c) X-ray diffraction spectrum of pristine MNPs. (d) XPS spectrum of pristine MNPs. (e) FT-IR spectra upon surface modification of MNPs: (i) MNPs@APS, (ii) MNPs-G1, and (iii) MNPs-G2. (f) Thermogravimetric analysis curves of (a) MNPs-APS, (b) MNPs-CC1, (c) MNPs-G1, (d) MNPs-CC2, and (e) MNPs-G2.

improved intrinsic mechanical properties of the polymer, which allows new opportunities to tailor advanced performance through magnetically tunable polymerization under mild and hazard-free conditions.

## RESULTS AND DISCUSSION

MNPs-G2@Cu<sup>2+</sup> co-nanoinitiators were designed following the concept of core–shell structure as illustrated in Scheme 1b. First, the core–shell MNPs@SiO<sub>2</sub> NPs were synthesized by

using a thermal decomposition method,<sup>32</sup> and subsequently, the surface was modified via silanization<sup>33</sup> with tetraethyl orthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APS). Second, cyanuric chloride (CC) was further functionalized with APS on the shell to create the triazine dendrimer (TD). Then, ethylenediamine (en) was introduced to form the branches of the dendrimer, the so-called first-generation dendrimer (G1),<sup>34</sup> namely MNPs-G1. To obtain the second generation (G2), the reaction was similarly repeated but with



Figure 2. XPS spectra of N 1s (left) and C 1s (right) dendrimer modifications (a) MNPs@APS, (b) MNPs-G1, and (c) MNPs-G2.

addition of CC and en, affording MNPs-G2. The so-called MNPs-G2 was covalently coordinated with Cu(II) through the addition of Cu(OAc)<sub>2</sub> on dendrimer branches, namely MNPs-G2@Cu<sup>2+</sup>.

The well-dispersed spherical MNPs with the diameter range of 15-21 nm were confirmed using the high-resolution TEM micrograph as depicted in Figure 1a. The X-ray diffraction pattern (Figure 1c) of synthesized MNPs corresponded to the (220), (311), (400), (422), (511), and (440) planes, which matched well with the crystal structure of magnetite (Fe<sub>3</sub>O<sub>4</sub>, JCPDS Card No. 85-1436).

To evaluate the presence of other minute phases, X-ray photoelectron spectroscopy (XPS) was used to identify and

quantify the chemical states of iron. The synthesized MNPs were further investigated by XPS as demonstrated in Figure 1d. The fitting signals illustrated two repeating patterns, which represented the higher binding energy fitted from Fe 2p1/2 and lower binding energy fitted from Fe 2p3/2. Both Fe 2p1/2 and 2p3/2 fitting patterns exhibited three main peaks and a satellite signal. Because of the less intense and broader peak of the satellite signal from the sample, the Fe 2p spectrum was fitted to only a single satellite peak of Fe<sup>3+</sup> as depicted in Figure 1d at 732.07 and 718.77 eV for the 2p1/2 and 2p3/2 spin—orbit components, respectively.<sup>35,36</sup> The lowest-binding energy peak at 710.27 eV and that at 723.47 eV were ascribed to Fe<sup>2+</sup> signals. The Fe<sup>3+</sup> signals were found in both octahedral species at 725.17



Figure 3. TEM-EDX micrographs of MNPs-G2@Cu<sup>2+</sup> co-nanoinitiators. The sample was prepared on a nickel (Ni) grid for TEM-EDX characterization. The copper content of the MNPs-G2@Cu<sup>2+</sup> dispersion was measured by ICP-MS (130 mg L<sup>-1</sup>).

and 710.27 eV and tetrahedral species at 727.77 and 714.77 eV. These values are comparable with those in the literature.<sup>36–40</sup> The core level Fe 2p spectrum can be fitted with the model of bulk Fe<sub>3</sub>O<sub>4</sub>.<sup>36,40,41</sup> Quantitative XPS analysis revealed an Fe<sup>3+</sup>:Fe<sup>2+</sup> ratio of 3:2, which could be ascribed to the existence of Fe<sub>3</sub>O<sub>4</sub> as a major phase and FeO as a minor phase resulting from surface analysis and calculation (Figure S1 and Table S1). The existence of FeO and epitaxial growth of Fe<sub>3</sub>O<sub>4</sub> from the outermost layers toward the core of the iron oleate precursor via thermal decomposition.

The surfaces of MNPs were further modified with silane to enhance the functionality and improve the chemical stability through selective coating of TEOS on the surfaces of MNPs (MNPs@SiO<sub>2</sub>). Figure 1b illustrates the silica shell uniformly coated on the magnetic core with a thickness of  $\sim 6$  nm. The core-shell magnetic silica structure was further examined using FT-IR spectroscopy. The FT-IR spectrum of MNPs@APS (spectrum i of Figure 1e) revealed a broad signal of an O-H symmetrical and asymmetrical stretching vibration band at  $3300-3400 \text{ cm}^{-1}$ . The vibration mode of water was found at 1647  $\rm cm^{-1}$  . The key bonding of the silica modification (between TEOS and APS) was confirmed by the existence of a strong Si-O-Si band at ~1096 cm<sup>-1.42,43</sup> Meanwhile, the Fe-O signal was weak but still visible in the spectrum (spectrum i of Figure 1e and Figure S2). This indicated the successful silane modification on MNPs. The FT-IR spectrum of MNPs-CC1 (the precursor of MNPs-G1) and MNPs-CC2 (the precursor of MNPs-G2) showed a C-Cl signal at 800 cm<sup>-1</sup> and a C=N (triazine) signal at 1630  $\text{cm}^{-1}$  (Figure S4), which are consistent

with the structures in Figure S3. In addition to the signals on FT-IR spectra mentioned above, the triazine signal (C=N), which was ascribed to the triazine moieties<sup>44,45</sup> on MNPs, was found in both MNPs-G1 (spectrum ii of Figure 1e) and MNPs-G2 (spectrum iii of Figure 1e) spectra at ~1639 and ~1659 cm<sup>-1</sup>, respectively. Moreover, the intensity ratio of C=N to Si-O-Si of MNPs-G2 was higher than that of MNPs-G1, which can be attributed to the growth of the G2 dendrimer on MNPs.

To examine the organic moieties in terms of the dendrimer modification at each generation, the results of thermogravimetric analysis (TGA) and elemental analysis (EA) clearly supported the sequence of dendrimer growth from G1 to G2 (Figure 1f and Tables S2 and S3). According to TGA, the level of decomposition of organic moieties on MNPs increased with each generation of dendrimer growth.<sup>34,46</sup> The organic moieties were decomposed in two steps. The first organic decomposition occurred at 150-250 °C, and the second occurred above 250 °C. The first step could be attributed to the loss of moisture. The second step could be attributed to the loss of organic moieties on the surface of the materials (APS, triazine, and diamine groups). The observed total weight losses of MNPs-APS, MNPs-CC1, MNPs-G1, MNPs-CC2, and MNPs-G2 were 15.43, 20.63, 25.45, 26.60, and 32.67 wt %, respectively. These TGA data indicated the yield of surface modification at each step as shown in Table S2. The weight loss of MNPs-G2 from TGA was in good agreement with the detected organic content from elemental analysis (EA) as reported in Tables S2 and S3.

To further prove the sequence of dendrimer growth on the surface of MNPs, the MNPs@APS, MNPs-G1, and MNPs-G2 samples were analyzed by XPS as illustrated in Figure 2. The

adventitious C 1s (C-C) feature at 284.80 eV was fixed to calibrate the spectra for interpretation. The C 1s and N 1s XPS spectra provided substantial details of dendrimer modifications. The C 1s envelope of MNPs@APS (-NH<sub>2</sub>) consisted of the characteristic binding energy from amines (C-N) around 286.00 eV, which confirmed amine modification on MNPs. A trace of adventitious carbon contamination (O-C=O and N-C=O) was detected at 288.11  $eV_{1}^{47}$  which was commonly exposed on the surface of the materials. With regard to G1 modification, the presence of protonated amines  $(C-NH_3^+)$ , carbon atoms in the triazine ring,48 and adventitious carbon (O-C=O and N-C=O) was seen around 286.15, 287.75, and 288.50 eV, respectively. The slightly broader signal<sup>49</sup> at 286.00 eV in the C 1s spectrum of MNPs-G2 was ascribed to the integration between the amine signal and protonated amine signal after further introduction of G2 dendritic structure (Figure S5). The XPS spectra of precursors (MNPs-CC1 and MNPs-CC2) are also characterized and discussed in the Supporting Information (Figure S6).

In accordance with the chemical environment from the N 1s spectra, the spectra of MNPs@APS, MNPs-G1, and MNPs-G2 showed the contribution of amine  $(R-NH_2, \sim 399 \text{ eV})$  and protonated amine  $(R-NH_3^+, \sim 401 \text{ eV})$  signals.<sup>50</sup> Meanwhile, the additional signal of sp<sup>2</sup>-hybridized N (C-N=C) around 398 eV,<sup>51,52</sup> which was the characteristic binding energy of the triazine ring, was corroborated by both MNPs-G1 and MNPs-G2 spectra. Furthermore, the successful modification of the dendritic structure from G1 to G2 is noteworthy with the ratio of the peak area from the N/C ratio of the triazine ring, as well as the N (triazine, ~398 eV) to N (dendrimer branches,  $-NH_2$ , ~399 eV) ratio (Figure S7).

Nevertheless, after dendrimer modification, the signal of the magnetic core (Fe 2p) was not detected in the XPS spectrum (Figure S8) due to the thickness of the modified shell (~13 nm). According to the higher generation of the dendrimer, the number of amino groups on terminal branches increased exponentially with each generation of growth, which allowed multiple reactive sites for the self-assembly of Cu(II) toward electrostatic interaction.<sup>7,53</sup>

The MNPs-G2@Cu<sup>2+</sup> core-shell structure was investigated by TEM-EDX. The diameter was 31 nm, after the immobilization of copper on MNPs-G2. From this analysis, dendrimer growth was evidenced by the layer being thicker than the coreshell MNPs@SiO<sub>2</sub> structure. From the TEM-EDX micrograph (Figure 3), it was found that the immobilization of copper considerably improved the dispersion of MNPs-G2 co-nanoinitiators because of the electrostatic repulsion of Cu<sup>2+</sup> on those branches from the dendrimer. Furthermore, TEM-EDX showed that the iron (Fe) content was notably at the magnetic core while silica (Si), oxygen (O), and nitrogen (N) contents were localized around the MNPs. The distribution of copper (Cu) content was evenly detected on MNPs-G2@Cu2+ co-nanoinitiators. Moreover, the copper content of MNPs-G2@Cu<sup>2+</sup> conanoinitiators was measured by ICP-MS analysis (130 mg L<sup>-1</sup> MNPs-G2@ $Cu^{2+}$  co-nanoinitiators).

Vibrating sample magnetometer (VSM) measurement revealed the magnetic properties of pristine MNPs and MNPs-G2@Cu<sup>2+</sup> co-nanoinitiators (Figure 4). The VSM measurement was carried out at room temperature from -10000 to 10000 Oe. The superparamagnetic behavior<sup>54–57</sup> was observed from both magnetization curves. Neither coercivity nor remanence was found.<sup>58</sup> The saturation magnetizations ( $M_s$ ) of magnetic nanoparticles (MNPs) before and



Figure 4. VSM measurement of MNPs before and after modification with the dendrimer.

after surface modification were 14.75 and 1.50 emu  $g^{-1}$ , respectively. The magnetization of synthesized MNPs via the thermal decomposition method in this work was consistent with the literature.<sup>56</sup>

 $M_{\rm s}$  decreased after the surface modification of silica and the dendrimer on MNPs. The lower saturation magnetization is attributed to the partial surface oxidation of MNPs,<sup>59</sup> the effect of other coatings,<sup>60</sup> the adsorption of surfactant molecules<sup>61</sup> on the surface of the particles, and/or the solvent<sup>62</sup> used to suspend the particles. These factors conceivably contributed to the canting angle of the magnetic moment in the crystal lattice. However, the modified magnetic co-nanoinitiators (MNPs-G2@Cu<sup>2+</sup>) are still responsive to an external magnetic field. According to characterizations presented above, it is confirmed that MNPs-G2@Cu<sup>2+</sup> co-nanoinitiators were successfully synthesized. The so-called MNPs-G2@Cu<sup>2+</sup> co-nanoinitiators represented the advanced nanoarchitecture design with the unique advantage of having a magnetic field response.

The polymerization of the TRIEGMA monomer was initiated in the presence of copper with *tert*-butyl peroxybenzoate. The amounts of copper introduced into the control polymerization system [Cu(OAc)<sub>2</sub>] and the MNPs-G2@Cu<sup>2+</sup> polymerization system were the same (0.249  $\mu$ mol). The copper content of the MNPs-G2@Cu<sup>2+</sup> was analyzed by ICP-MS. Commercial Cu(OAc)<sub>2</sub> was stoichiometrically introduced directly into the control system. Figure S9 shows the digital image of the cured polymer in a vial. This clearly shows that, in the absence of a Cu source, the polymerization did not occur after curing for the same duration. The redox-initiated radical polymerization was essentially promoted in the presence of a Cu source.

The monomer conversions (Figure 5) of the MNPs-G2@  $Cu^{2+}$  and  $Cu(OAc)_2$  systems are relatively comparable, when the duration of polymerization reaches 24 h. Conversely, the monomer conversion from Fe<sub>3</sub>O<sub>4</sub> is consistently low. The improvement in the monomer conversion from the MNPs-G2@  $Cu^{2+}$  system was likely attributed to the good dispersion of copper on magnetic dendrimer co-nanoinitiators. The redox reaction between Cu(II) and Cu(I) was therefore synergistically evenly promoted by the decomposition of peroxide species to initiate redox radical polymerization in the system. A plausible radical production mechanism of MNPs-G2@ $Cu^{2+}$  co-nanoinitiators is proposed in Figure S10. Consequently, it is reasonable to confirm that MNPs-G2@ $Cu^{2+}$  co-nanoinitiators



**Figure 5.** Illustration of the conversion of the monomer with different initiators: (black squares)  $Cu(OAc)_2$  (control), (blue triangles) MNPs-G2@Cu<sup>2+</sup>, and (red circles) Fe<sub>3</sub>O<sub>4</sub>.

played the crucial role during polymerization. Moreover, MNPs- $G2@Cu^{2+}$  could initiate polymerization with other C=C bondcontaining monomers, such as 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate (HEA), and ethylene glycol dimethacrylate (EGDMA) as depicted in Figure S11.

Upon application of an external magnetic field (NdFeB magnet, 0.2-0.5 T) following the concept depicted in Figure 6a, the resulting magnetically induced accumulation of MNPs-G2@  $Cu^{2+}$  co-nanoinitiators enabled the selected area (Figure 6b) to undergo redox-initiated radical polymerization. The location with a high loading of MNPs-G2@Cu<sup>2+</sup> (directed by the external permanent magnet) showed a higher degree of polymerization on the right side, while the left side showed little reaction, was still in liquid form, and could be removed by an organic solvent after 1.5 h. Additionally, the monomer conversion was determined by FT-IR (Figure 6c) from the experiment depicted in Figure 6b. The polymerization under a magnetic field treatment is also depicted in Figure S12. The mechanical properties from the resulting polymer were investigated herein. Tensile tests of the anaerobic polymer initiated by  $Cu(OAc)_2$  and MNPs-G2@Cu<sup>2+</sup> were conducted to compare the mechanical properties (Figure 7a,b).

The mechanical parameters from the tensile test depicted in panels a and b of Figure 7 are presented in Table 1. It is noteworthy that the MNPs-G2@Cu<sup>2+</sup> polymerization (without a magnetic field applied) system exhibited a remarkable improvement in its Young's modulus, toughness, and tensile strength (stress), while elongation (strain) was relatively consistent compared with that of the control system. The mechanical improvement of the MNPs-G2@Cu<sup>2+</sup> system was ascribed to the higher density of chemical cross-linking of the methacrylate functional group because the enhancement of



**Figure 6.** (a) Illustration of the MNPs-G2@ $Cu^{2+}$  co-nanoinitiators directed by an external magnetic field for localized polymerization at room temperature for 1.5 h. (b) Comparison of the polymer in the presence of MNPs-G2@ $Cu^{2+}$  co-nanoinitiators with lower (left) and higher (right) degrees of polymerization inside the glass Petri dish (top view). The magnet underneath was subsequently removed after directing the MNPs-G2@ $Cu^{2+}$ . (c) Monomer conversion from the experiment shown in panel b.



**Figure 7.** Tensile stress-strain curve of the free-standing form of polymerized TRIEGMA with (a)  $Cu(OAc)_2$  as a control system and (b) MNPs-G2@  $Cu^{2+}$ . (c) Comparison of adhesion between the MNPs-G2@ $Cu^{2+}$  and control system by a single-lap shear test with 15 samples. (d) Photograph of the failure of the adhesive at the bonding area of the MNPs-G2@ $Cu^{2+}$  system after it had been pulled apart. (e) Diagram of chemical cross-linking and physical interaction formed by random entanglement and then dissipated by chain disentanglement after the system had been pulled apart.

Table 1. Mechanical Parameters Calculated from Tensile Tests Represented in Panels a and b of Figure 7

sample	Young's modulus (MPa)	toughness (MJ m <sup>-3</sup> )	tensile strength (MPa)	elongation at break (%)
TRIEGMA-Cu(OAc) <sub>2</sub>	$62.64 \pm 0.06$	$0.15 \pm 8.07$	$4.70 \pm 0.37$	$6.78 \pm 0.13$
TRIEGMA-MNPs-G2@Cu <sup>2+</sup>	181.42 $\pm 0.04$	$0.37 \pm 7.70$	$12.00 \pm 1.18$	$6.00 \pm 0.15$

radical species from peroxide was promoted by the redox reaction of MNPs-G2@Cu<sup>2+</sup>, resulting in stronger entanglement

of polymer chains. Reasonably, the chemical cross-linking dominantly contributed to the major mechanical improvement

in the Young's modulus, toughness, and tensile strength compared with those of the control system.

Meanwhile, the physical interactions were attributed to van der Waals, London dispersive, H-bond, and ion-dipole interactions between the G2 dendrimer branches (amine functional group) and the polymer chains, resulting in the generation of sacrificial bonds to dissipate energy.<sup>63,64</sup> Hence, the slight change in tensile elongation at the breaking point suggested strong chemical cross-linking was effectively formed, while an only small contribution to energy dissipation was observed.<sup>63</sup> Moreover, the presence of MNPs-G2@Cu<sup>2+</sup> in the polymer system provided the high tensile strength with the restriction of elongation, which indicated the characteristic behavior of thermoset. Thus, MNPs-G2@Cu<sup>2+</sup> is considerably effective as co-nanoinitiators and nanofillers, which strengthen the mechanical performance of the polymer via either chemical cross-linking or physical interactions.

The interfacial adhesion of cured TRIEGMA was carried out by using a single-lap shear strength test to evaluate the adhesive property. The bonding areas between the adherends of both systems (MNPs-G2@Cu<sup>2+</sup> and control) were physically secured under deoxygenated conditions with a 24 h polymerization time without a trace of wet adhesive leftover. Typically, anaerobic adhesives are preferably used on an active metal surface, such as steel or aluminum substrates, to achieve faster curing.<sup>65</sup> Therefore, in this work, the anaerobic adhesive was applied on the steel substrate for further experimental investigations.

According to Figure 7c, the adhesive strength of the control and the MNPs-G2@Cu<sup>2+</sup> system was measured and analyzed using 15 samples for each system. The maximum lap shear strengths from the control and MNPs-G2@Cu<sup>2+</sup> system were 164 and 117 MPa, respectively. The sawtooth appearance<sup>66</sup> on the shear stress—strain curve (Figure S13a) was attributed to the poorer uniformity of adhesive bonding of the control system compared with that of the MNPs-G2@Cu<sup>2+</sup> adhesive system (Figure S13b). Moreover, strain hardening<sup>63</sup> was detected from the shear stress—strain curves of the control adhesive during the lap shear strength measurement, suggesting that the covalent cross-linking was further deformed across an elastic barrier, and necking behavior was therefore detected. This result indicated that the strain of the control system was higher at certain shear stress values compared with the MNPs-G2@Cu<sup>2+</sup> adhesive system.

This is because the MNPs-G2@Cu<sup>2+</sup> adhesive system provided a higher cross-linking density; therefore, the breaking at strong lap shear strength with short elongation was found at the breaking point, which corresponded with the more brittle behavior obtained by the tensile test. Consequently, the slope of the shear stress-strain curve from the MNPs-G2@Cu<sup>2+</sup> adhesive sample increased constantly without strain hardening until failure was detected.

According to the different behaviors of the MNPs-G2@Cu<sup>2+</sup> and control adhesive, there is strong evidence to prove that MNPs-G2@Cu<sup>2+</sup> has impacted the polymerization system as nanofillers for tailoring the intrinsic property and serving as the co-nanoinitiators. The MNPs-G2@Cu<sup>2+</sup> adhesive sample (Figure 7d) demonstrated adhesive failure, where the failure occurred between the brittle adhesive and substrate. This reflects the fact that the physical interaction, including Hbonding, electrostatic interaction, or London dispersion, contributed to the failure of lap shear strength following the suggested mechanism depicted in Figure 7e.<sup>64</sup> In other words, the MNPs-G2@Cu<sup>2+</sup> adhesive could resist the shear force during testing, so that the residual adhesive remained on one substrate surface. With regard to lap shear testing, the maximum lap shear strength of the MNPs-G2@Cu<sup>2+</sup> adhesive is not as high as that of the control adhesive. However, it is higher than or comparable to those of most commercial anaerobic adhesives<sup>67–69</sup> with the additional advantage of localized curing of the adhesive.

## CONCLUSION

In summary, MNPs-G2@Cu<sup>2+</sup> co-nanoinitiators were successfully developed from the tunable core MNPs with a desirable dendrimer shell to serve as magnetic co-nanoinitiators and nanofillers. The localized redox-initiated free radical polymerization of the anaerobic adhesive was triggered by the synergistic system of initiators of MNPs-G2@Cu<sup>2+</sup> and peroxide. Moreover, the presence of MNPs-G2@Cu2+ effectively provided superior mechanical properties compared with those of the control system with respect to denser chemical cross-linking and physical interaction. However, the mechanical properties of the resulting polymer under the applied magnetic field still require further development to achieve its promising outcome. The designed nanoinitiators of core-shell MNPs-G2@Cu<sup>2+</sup> could open new pathways for concurrently reinforcing mechanical properties and realizing the magnetically initiated localized polymerization. This work is potentially attractive in the aerospace, chemical, electronics, and medical industries, where air-sensitive conditions and adhesive formation are required.

## EXPERIMENTAL SECTION

Synthesis of Magnetic Nanoparticles (MNPs). Spherical magnetic nanoparticles (expected size of 25-30 nm) were synthesized via a thermal decomposition method developed by Park et al.<sup>24</sup> Briefly, an iron oleate precursor was prepared by refluxing the reaction mixture of 2.16 g (8 mmol) of iron chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), and 7.30 g (23 mmol) of sodium oleate dissolved in 16 mL of ethanol (EtOH), 12 mL of deionized (DI) water, and 28 mL of hexane. The solution was heated to 70 °C for 4 h. The iron oleate precursor was purified by extraction several times with DI water and further evaporated with mixed solvents. The waxy form was obtained as an iron oleate precursor. Then, the iron oleate precursor, oleic acid (OA), and 1-octadecene [36:5.7:200 (w/ w)] were mixed at room temperature. The reaction mixture was heated to 320 °C at a constant rate of 3.3 °C min<sup>-1</sup> for 30 min under inert conditions using the Schlenk technique. A severe reaction was occurred, and the solution appeared turbid and brownish black. After the resulting solution with MNPs was cooled to room temperature, hexane and isopropanol were used to precipitate MNPs. The MNPs were separated by centrifugation and redispersed in cyclohexane.

Preparation of Magnetic Surface Modifications with 3-Aminopropyltriethoxysilane (MNPs@APS). To improve the functionality of bare MNPs, silane modification was introduced to attach the proper linkers to the surface. MNPs were coated with a silane compound using the following procedure. First, 9.88 g (22 mmol) of Igepal CO-520 and 90 mL of anhydrous cyclohexane were stirred together for 10 min. Subsequently, 1.50 mL of 25% ammonium hydroxide (NH<sub>4</sub>OH) was gradually mixed before the addition of 90 mg of MNPs to the solution. Then, 600 mL of tetraethyl orthosilicate (TEOS) was added dropwise, and the mixture stirred for 16 h at room temperature. The resulting core-shell MNPs@SiO2 NPs were purified by being washed with ethanol, centrifuged, and redispersed in ethanol. In this way, the thickness of the silica shell coated on MNPs was approximately 5-6 nm. To modify the amine group on MNPs@SiO<sub>2</sub> NPs, APS was used as the coupling agent. Thirty milligrams of MNPs@ SiO<sub>2</sub> core-shell NPs was dispersed well in a mixture of H<sub>2</sub>O and EtOH (1:1) by sonication before the addition of 50  $\mu$ L of APS in the following step. The reaction mixture was continuously stirred for 8 h at room temperature under an inert atmosphere. The resulting MNPs@APS

NPs were purified with ethanol and separated by centrifugation. Then, MNPs@APS ( $MNPs@NH_2$ ) can be redispersed and sonicated in THF for further modifications.

Preparation of the Magnetic Triazine Dendrimer (MNPs-**G2@Cu<sup>2+</sup>).** To promote the surface functionality, the dendrimer ligand was grafted onto MNPs@APS NPs. First, 1.85 g (10 mmol) of cyanuric chloride (CC) and 1.40 mL of trimethylamine were dissolved in THF. Subsequently, 2 g of MNPs@APS was dispersed inside the prior solution to initiate the amine coupling reaction, and the reaction mixture was stirred for 10 h (named MNPs-CC1). The resulting MNPs-CC1 were centrifuged and purified several times with hot THF. Next, the dispersion of 1 g of MNPs-CC1 in 12 mL of DMF, 0.53 mL of ethylenediamine, and 1.1 mL of triethylamine was mixed at 60 °C for 12 h [named generation 1 (G1) of MNPs (MNPs-G1)]. The resulting MNPs-G1 were centrifuged and purified several times with hot ethanol. The second generation of the dendrimer was prepared correspondingly with the first generation. MNPs-CC2 were synthesized by stirring the slurry of 1 g of MNPs-G1, 1.66 g of cyanuric chloride, and 1.2 mL of triethylamine in 20 mL of THF for 14 h (named MNPs-CC2). The resulting MNPs-CC2 were centrifuged and purified several times with hot THF. After that, the suspension of 1 g of MNPs-CC2 in 20 mL of DMF was supplemented with 0.63 mL of ethylenediamine and 1.3 mL of triethylamine. The MNPs-G2 were formed after the reaction mixture had been stirred at for 60 °C for 14 h and then washed with hot ethanol. The MNPs-G2 were redispersed in DMF for immobilization of copper(II) in the following step. To immobilize the copper(II) on the dendrimer ligand, the dispersion of 0.5 g of MNPs-G2 in 10 mL of DMF was mixed with 0.09 g ( $\overline{0.7}$  mmol) of Cu(OAc)<sub>2</sub>, and the mixture was stirred for 6 h. The suspension of MNPs-G2@Cu<sup>2+</sup> (dark green) was subsequentially washed with acetone and stored in the fridge.

**Preparation of the Adhesive Formula.** The anaerobic polymerization was performed as follows. TRIEGMA (1.53 mmol), *tert*-butyl peroxybenzoate (98% peroxide, 0.21 mmol), and a copper(II) source (0.249  $\mu$ mol) were mixed using a polymerization system. The concentration of Cu(II) on MNPs-G2@Cu<sup>2+</sup> co-nanoinitiators was analyzed using ICP-MS. For the control system, Cu(OAc)<sub>2</sub> was utilized as the copper source by weighing the copper salt into the polymerization system, replacing the co-nanoinitiators. For both control and MNP systems, all components were mixed and cured at room temperature in a deoxygenated environment for 24 h.<sup>70</sup>

**Method for Monitoring the Monomer Conversion by FT-IR.** A droplet of the reactive adhesive formula (with or without magnetic nanoparticles) was used to characterize monomer conversion over time via an FT-IR spectrometer. The sample was prepared by the combination of the TRIEGMA monomer (1.53 mmol), peroxide (0.21 mmol), and an initiator  $[\text{Fe}_3\text{O}_4, \text{Cu}(\text{OAc})_2, \text{ or MNPs-G2}(2000)^2)$  or MNPs-G2(2000) Cu<sup>2+</sup>]. The loadings of metal ion of pure MNPs (Fe<sub>3</sub>O<sub>4</sub>)-iron (Fe), Cu(OAc)<sub>2</sub>, and MNPs-G2(2000)<sup>2+</sup>-copper (Cu) were equivalently prepared with 0.249  $\mu$ mol in the polymerization system. The signal at 1637 cm<sup>-1</sup> represented the C=C bond of TRIEGMA, which was monitored and used to calculate the conversion of the monomer over time. The lower absorbance of the vinyl monomer (C=C bond at 1637 cm<sup>-1</sup>) indicated the higher degree of conversion of the TRIEGMA monomer. The percentage of conversion can be calculated from eq 1:

$$\% \text{ conversion} = \frac{A(0) - A(t)}{A(0)} \times 100 \tag{1}$$

where A(0) and A(t) represent the absorbance at 1637 cm<sup>-1</sup> at time zero and time *t*, respectively.

**Method for the Tensile Test.** The reactive mixture of the adhesive formula was cured on the Teflon mold in a rectangular shape. The polymerization occurred in a deoxygenated environment (glovebox) at room temperature for 24 h. After that, the sample was treated with a hot air gun (100 °C) to obtain the free-standing form. Finally, a specimen with a width of 15 mm, a thickness of 1 mm, and an initial nominal gauge length of 10 mm (length between the grippers of the mechanical tester) was obtained. The tensile stress–strain test was conducted by using a mechanical tester (MTS Criterion, model 43) with a load cell (1 kN) and strain rate of 1.27 mm min<sup>-1</sup> at room temperature. The stress

was calculated with respect to the equation  $\sigma = F/A$ , where *F* is the load and *A* is bonding area of the adhesive. The strain was considered from the equation  $\varepsilon = \Delta L/L$ , where  $\Delta L$  is the elongation of the sample compared with the initial length (*L*) of the sample. Young's modulus was acquired from the slope at the beginning of the stress–strain curve (linear region).

**Method for the Single-Lap Shear Adhesion Test.** The surface of the stainless-steel substrates (25 mm in width × 102 mm in length × 2 mm in thickness) was cleaned with isopropanol as a surface pretreatment. To control the thickness of the adhesive  $(160-170 \ \mu m)$  between adherends, the stainless-steel substrate was framed by double-sided tape on the rough side. The reactive mixture of the adhesive formula was applied to the bonding area (20 mm in width × 13 mm in length), which was secured by using a clip. The panels were treated overnight under a deoxygenated environment without temperature applied. The lap shear test was conducted by using mechanical tester (MTS Criterion, model 43) with a load cell (1 kN) and strain rate of 1.27 mm min<sup>-1</sup> at room temperature.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c08040.

Materials and instrument, Fe 2p XPS spectra of MNPs, C 1s and N 1s XPS spectra and calculation of dendrimer modification, TGA and EA of the magnetic triazine dendrimer, digital photo of the starting materials combined in the polymerization system, spatial resolution investigation, plausible mechanism of polymerization, and lap shear strength testing (PDF)

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## ABBREVIATIONS

MNPs, magnetic nanoparticles; APS, aminopropyltriethoxysilane; CC, cyanuric chloride; en, ethylenediamine; FT-IR, Fourier transform infrared; TEM, transmission electron microscopy; TRIEGMA, triethylene glycol dimethacrylate.

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