Supplementary Information

Synergistic enhancement of hydrogen storage and air stability via Mg nanocrystal-polymer interfacial interactions

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Experimental Details

Reagents and Materials. Bis(cyclopentadienyl) magnesium 99.99+% (Cp_2Mg) was purchased from Strem Chemicals. Lithium foil 99%, polystyrene (PS, M_W 123K) and low density polyethylene (PE) were purchased from Alfa Aesar. Poly(methyl methacrylate) (PMMA, M_W 120K), polylactic acid (PLA, M_W 60K) and naphthalene 99% were purchased from Sigma Aldrich. Tetrahydrofuran (THF) was freshly distilled before use.

Nanocomposite Synthesis. Mg-polymer nanocomposites were synthesized under argon atmosphere at room temperature. PMMA (0.90 g), PS (0.90 g), or PE (0.27 g) was dissolved in distilled tetrahydrofuran (THF, 45 mL) by magnetically stirring overnight. To aid PE dissolution, the THF solution was heated at 115 °C, then allowed to cool to room temperature. Cp_2Mg (2.31 g, 0.015 mol) was added to the polymer solution and stirred until completely dissolved. Separately, a lithium naphthalide solution was prepared. Naphthalene (1.80 g, 0.014 mol) was dissolved in THF (90 mL), followed by the addition of Li metal (0.135 g, 0.019 mol). The mixture was stirred until the lithium was completely dissolved, resulting in a dark green solution. Once fully dissolved, the polymer/Cp_2Mg solution was added to the lithium naphthalide solution, becoming turbid within minutes to yield dark grey flocculate. The reaction mixture was magnetically stirred overnight. The resultant product was separated from solution by centrifugation (9000 rpm, 20 min), cleaned with additional THF, and obtained by centrifugation (9000 rpm, 15 min). Nanocomposites were allowed to completely dry under Ar before exposure to ambient atmosphere.

It was found that PLA reacted with the organometallic precursor Cp_2Mg, terminating the reaction. To circumnavigate this obstacle, composites consisting of PLA were synthesized using a modified procedure: Cp_2Mg was dissolved in THF (15 mL), and added to the lithium naphthalide solution. After mixing for 30 seconds, a PLA/THF solution (0.90 g/30 mL) was added. To aid PLA dissolution, the THF solution was heated at 115 °C, then allowed to cool to room temperature.

To determine the maximum magnesium loading in PMMA while maintaining air stability, adjustments to the synthesis were made. *Caution: nano magnesium is highly reactive. Too little polymer* *coating will result in a pyrophoric product!* Nanocomposites were synthesized as described above using the following adjusted PMMA factors: 1.00 (0.900 g), 0.75 (0.675 g), 0.50 (0.450 g), 0.42 (0.378 g) and 0.30 (0.270 g).

Material Characterization and Instrumentation. Elemental analysis was performed with a Varian 720-ES inductively coupled plasma optical emission spectrometer (ICP-OES). The size and morphology of polymer matrix embedded Mg NCs were examined using a JEOL 2100F transmission electron microscope (200 kV). Specimens were prepared in an Ar atmosphere glovebox by depositing a drop of the reaction solution on a lacey formvar grid, followed immediately by multiple washings with THF and acetone. Nanocrystal morphology after hydrogen and thermal cycling was examined by TEM at 120 kV. Samples were embedded in optical grade epoxy resin (epo-tech 302) and fully cured at room temperature (~12 hours). Next the sample was mounted on a Leica EM UC7 microtome holder. The region of interest with the MgPMMMA piece was then trimmed into a trapezoid shape approximately 200 x 160 μm in size using a DIATOME Ultratrim 45 diamond trimming knife and sectioned using Ultra45 diamond knife with a water bath. The 20-50nm thick cross-section slices were collected on TEM grids from the water bath and coated with 2-5 nm thick amorphous carbon layer. X-ray diffraction patterns were obtained using a Bruker D8 Discover X-ray diffractometer with a general area detector diffraction system (GADDS) using Cu K_α radiation ($\lambda = 0.154$ nm). Thermal gravimetric analysis (TGA) was performed under Ar at a scan rate of 20 ºC/min using a TA Instruments Q5000IR. Simultaneously, mass spectra of evolved species were obtained with an attached Thermostar mass spectrometer running a bargraph scan set to cycle a range of 0-300 atomic mass units. Hydrogen absorption/desorption was performed with a HyEnergy PCT Pro-2000 instrument at 200/300 °C and 30/0 bar of H_2.

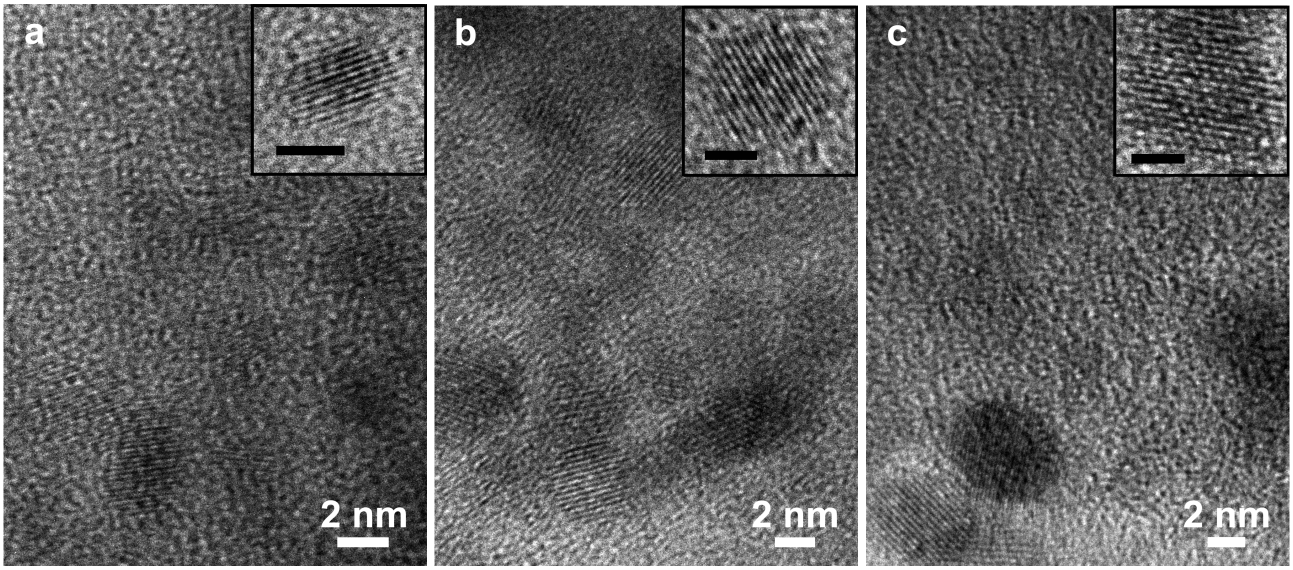

Figure S1. TEM images of MgPMMA nanocomposites containing a) 49, b) 54.7 and c) 58.2 wt. % Mg. Scale bars represent 2 nm.

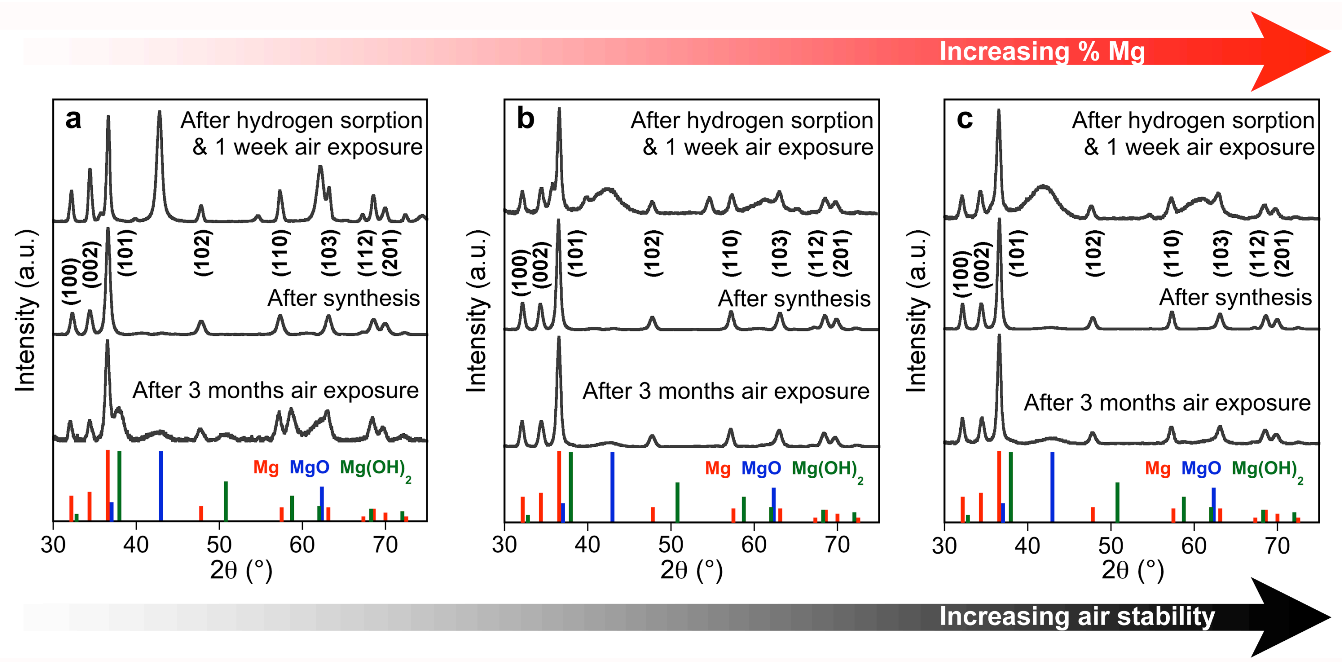

Figure S2. XRD spectra of MgPMMA nanocomposites after synthesis (middle trace), after 3 months air exposure (bottom trace), and after hydrogen sorption and subsequent air exposure for 1 week (top trace) for composites containing a) 49, b) 54.7 and c) 58.2 wt. % Mg.

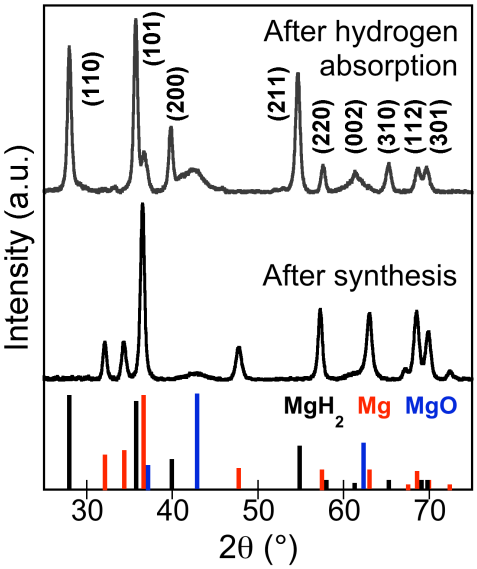

Figure S3. XRD spectra of a MgPMMA nanocomposite containing 60 wt. % Mg after synthesis (bottom trace) and after hydrogen absorption (top trace). The dominant diffraction peaks after hydrogen absorption are from MgH_2, with a small contribution due to Mg observed at 36.6°, and MgO at 42.9°.

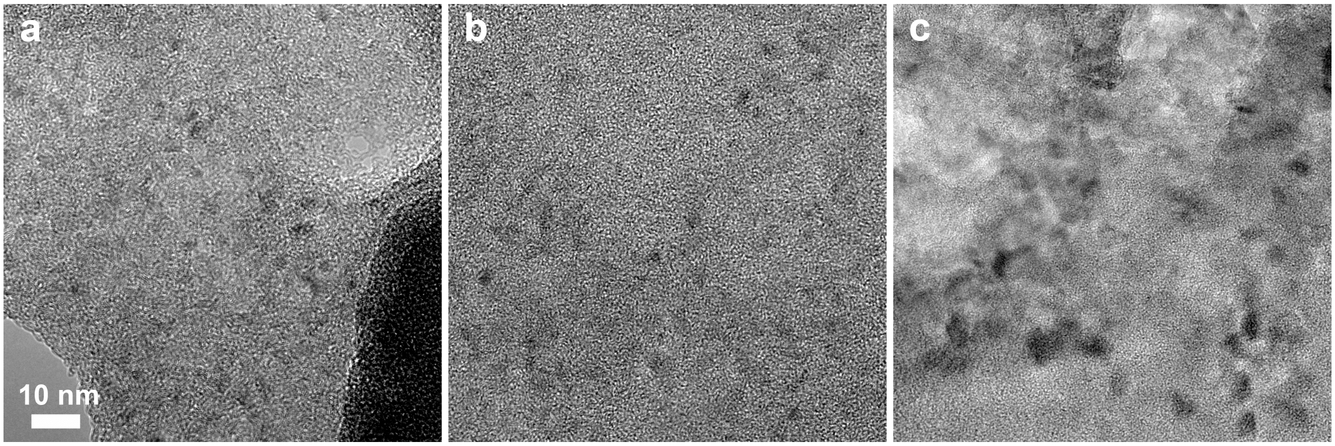

Figure S4. TEM images of microtomed slices of a MgPMMA nanocomposite (a) after synthesis and (b), (c) after hydrogen cycling. Overall the nanocrystal morphology is maintained (b), however isolated regions show evidence of particle coarsening (c).

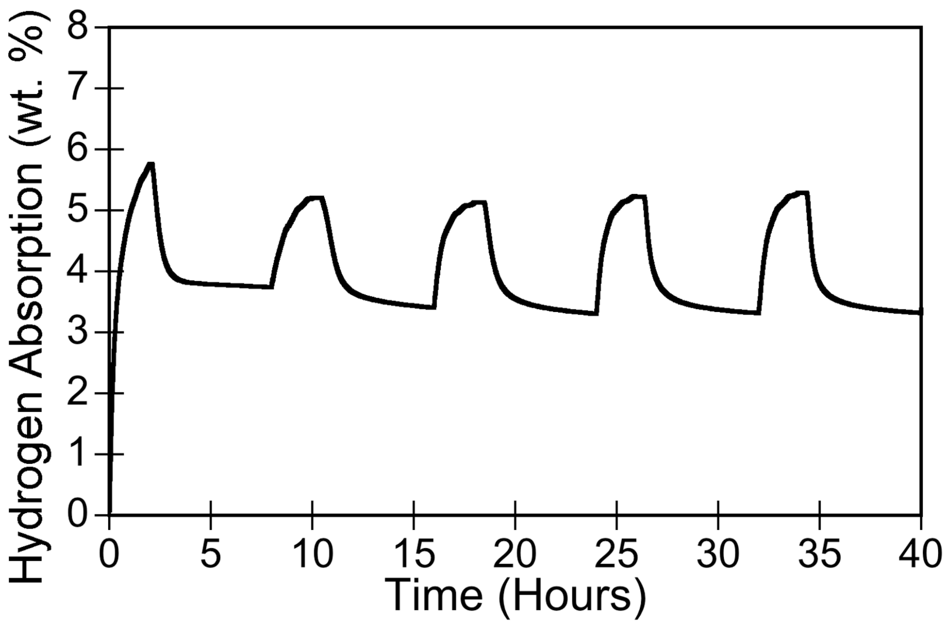

Figure S5. Hydrogen absorption (200 °C, 30 bar H_2) and desorption (300 °C, 0 bar H_2) cycling of a MgPMMA nanocomposite containing 60 wt. % Mg.

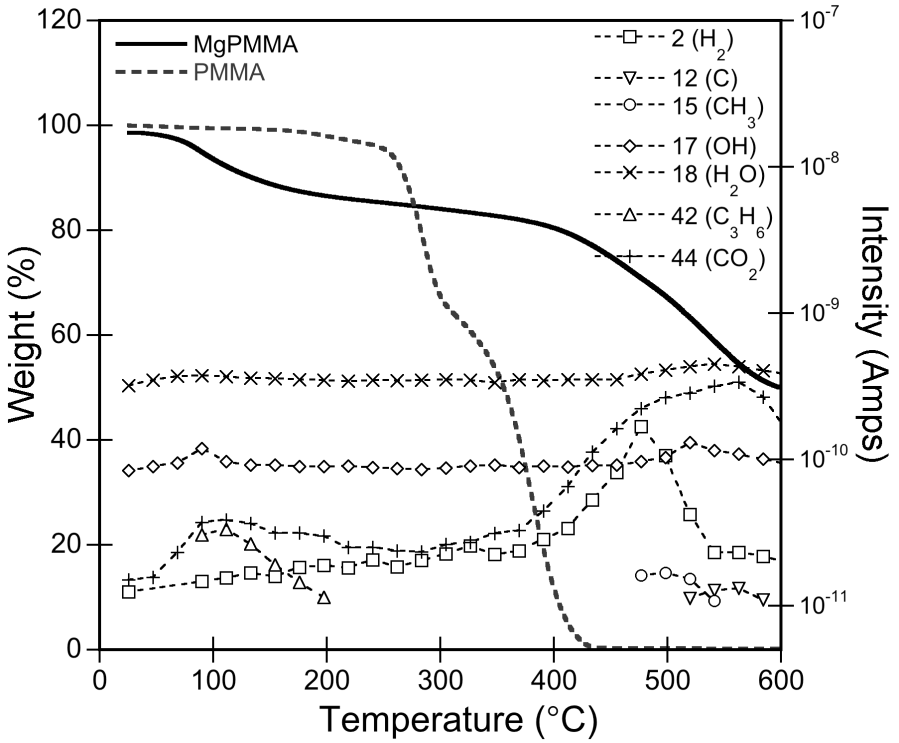

Figure S6. Thermal gravimetric analysis (TGA) of a MgPMMA nanocomposite (solid line). Notable evolved species measured by mass spectroscopy (MS) are included. The first weight loss is attributed to the removal of low molecular weight polymers, and the well studied thermal degradation of PMMA by cleavage of weaker C-C bonds at head-to-head linkages and terminal vinyl bonds. The second weight loss is attributed to random C-C scission and complete degradation of the PMMA matrix. Pure PMMA TGA trace is shown for comparison (dashed line).

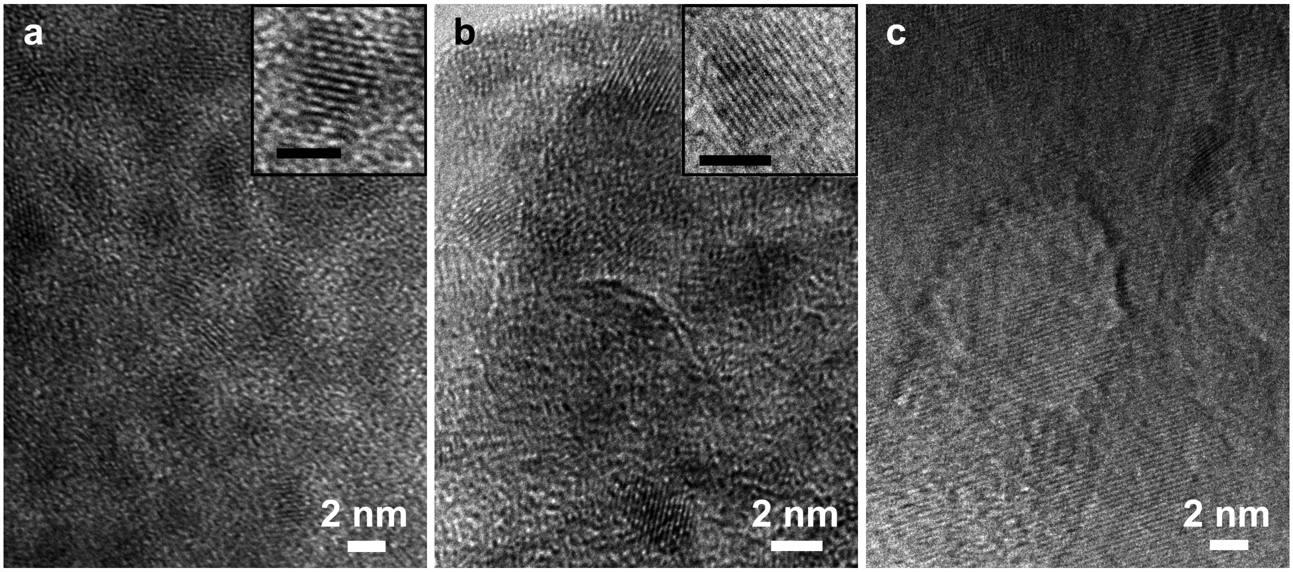

Figure S7. TEM images of Mg nanocomposites containing the polymer a) polyethylene, b) polystyrene and c) polylactic acid. Scale bars represent 2 nm.

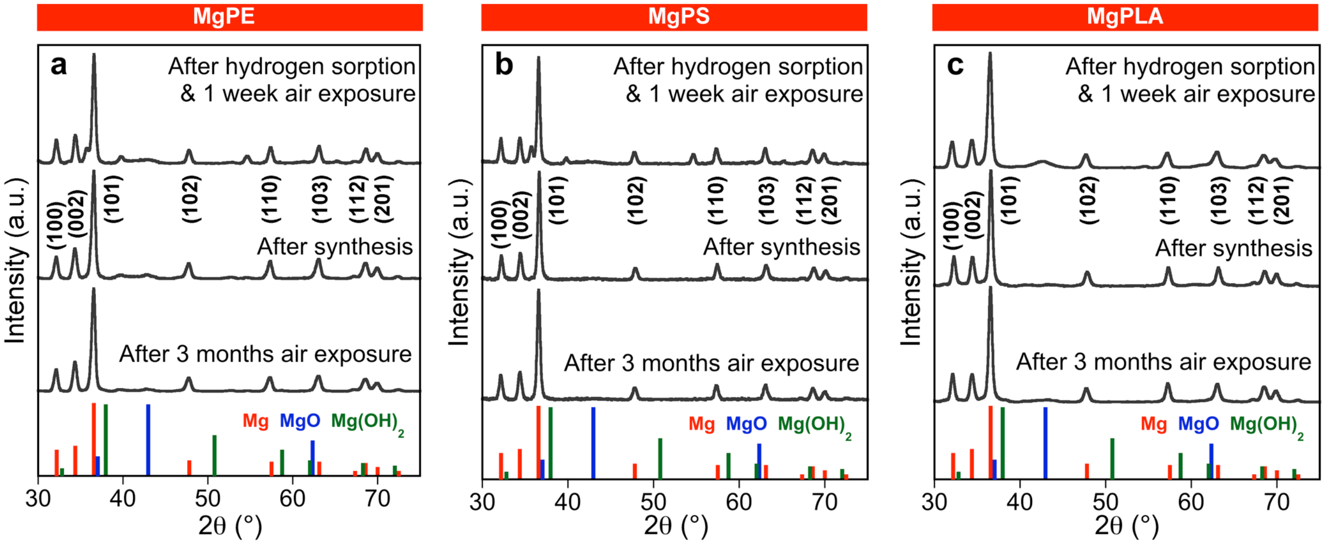

Figure S8. XRD spectra of Mg nanocomposites after synthesis (middle trace), after 3 months air exposure (bottom trace), and after hydrogen sorption and subsequent air exposure for 1 week (top trace) for composites containing the polymer a) polyethylene, b) polystyrene and c) polylactic acid.

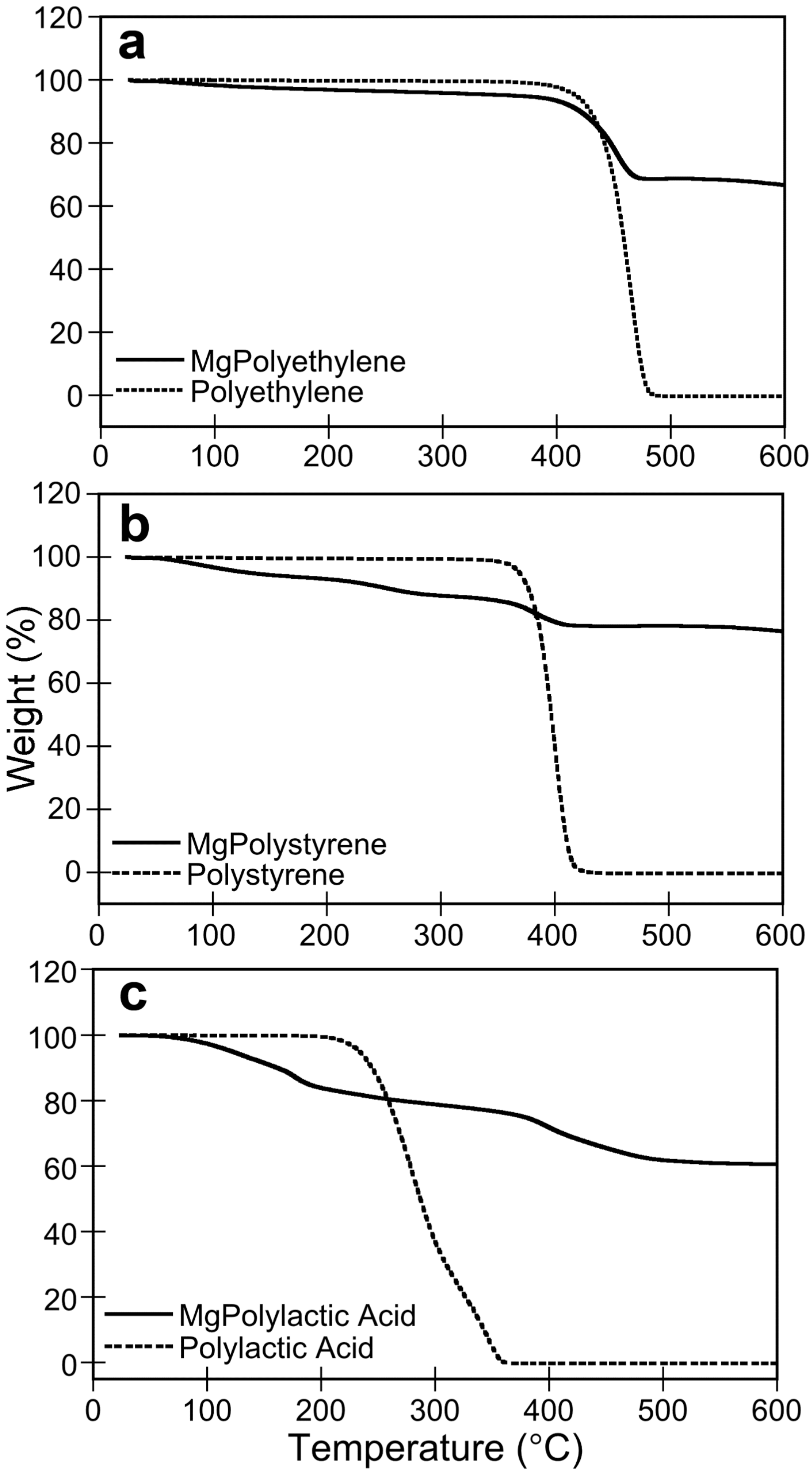

Figure S9. Thermal gravimetric analyses of composites containing the polymer a) polyethylene, b) polystyrene and c) polylactic acid. Pure polymer TGA trace is shown for comparison.

Table S1. Wt. and vol. % Mg, particle diameter and wt. % Mg hydrogen absorption of nanocomposites synthesized with different polymer.

Polymer	Wt. % Mg (ICP-OES)	Vol. % Mg (calc.)	Diameter, nm (TEM)	Hydrogen absorption, wt. %
Poly(methyl methacrylate)	65 ± 2	55.9	2.1 ± 0.5	6.95
Polyethylene	62 ± 5	44.5	2.8 ± 0.6	3.94
Polystyrene	77 ± 2	66.9	2.9 ± 0.8	5.63
Polylactic acid	65 ± 4	57.2	Large sheets	0.58