Electronic Supplementary Information

Magnetic responsive composites made from a sulfur-rich polymer

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General considerations

50-poly(S-*r*-canola) synthesis:

The copolymerisation of sulfur and canola oil was carried out as previously described.¹⁻⁵ For full experimental details of this polymer please synthesis and additional characterisation data refer to Worthington *et. al. Adv. Sustainable Syst.*, 2018, 2, 1800024 and other prior publications on the synthesis and applications of this polymer.¹⁻⁵

¹H Nuclear magnetic resonance (NMR) spectroscopy: Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a 600 MHz spectrometer. All chemical shifts are quoted on the δ scale in ppm using residual solvent as the internal standard (pyridine-D5: δ = 8.74).

Thermogravimetric analysis (TGA): TGA and DSC were carried out on a Perkin Elmer STA8000 simultaneous thermal analyser (STA). A sample size of approximately 10 mg was used. The furnace was purged at 20 mL/min with nitrogen and equilibrated for 1 minute at 30 °C before each run. The samples were heated up to 800 °C using a 20 °C/min heating rate. The temperature was held isothermally at 800 °C for 10 minutes at the end of each experiment.

Differential scanning calorimetry (DSC): DSC analysis was carried out on a Perkin Elmer DSC 8000 dynamic scanning calorimeter. For all polymer samples a mass of approximately 10 mg was used for analysis. For sulfur calibration, various amounts of sulfur were added. For analysis of T_g the temperature was initially held at 30 °C for 10 minutes to equilibrate the sample. Then the temperature was dropped down to -50 °C at a rate of 10 °C / minute. The temperature was then cycled back and forth between -50 and +50 °C three times at rate of 10 °C / minute. The temperature was then decreased back to 30 °C to end the run. For free sulfur content analysis all runs started by holding the temperature at 30 °C for 10 minutes to equilibrate the sample. The temperature was then increased to 150 °C at a rate of 10 °C / minute and held there for 2 minutes. The temperature was then dropped back to 30 °C to end the run.

Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy: Scanning Electron Microscopy (SEM) images were obtained using an FEI F50 Inspect system, while corresponding EDS spectra were obtained using an EDAX Octane Pro detector.

Powder X-ray diffraction analysis:

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance Eco diffractometer (Bragg-Brentano geometry) using Co-K α radiation ($\lambda = 1.78897$ Å). The Bragg angle (2 θ) was varied from 10° to 90° with a step size of 0.019°, measurement time of 0.45 s per step and sample rotation at 15 rpm. The XRD patterns were collected on a silicon low background sample holder, where powder samples were deposited onto the surface of the holder.

Infrared spectroscopy: Infrared (IR) spectra were recorded on a Fourier Transform spectrophotometer using the ATR method. Absorption maxima (v_{max}) are reported in wavenumbers (cm⁻¹).

Combustion analysis for elemental composition: CHNS analysis was carried out by the chemical analysis facility at Macquarie University. All samples were stored in a fridge before analysis. The 95% confidence interval of the technique for organic compounds is $\pm 0.3\%$ with a precision of $\pm 0.2\%$.

X-ray photoelectron spectroscopy (XPS):⁶ was performed with a SPECS instrument at a base pressure of a few 10^{-10} mbar in an ultra-high vacuum (UHV) chamber. A non-monochromatic X-ray source with a Mg anode (12 kV - 200 W, Ka line with an excitation energy of 1253.6 eV) was used for irradiation and a Phoibos 100 (SPECS) hemispherical analyser was used for recording spectrum. The angle between the X-ray source and the analyser is $54.7 \degree$. A survey scan with 40 eV pass energy was performed first and the high-resolution scans at a pass energy of 10 eV were recorded for characterizing the chemical states of a sample surface including chemical composition and valence state of element with a step size of 0.1 eV. Spectra were calibrated based on identifying C-C sp3 species to 285.0 eV.⁷ The relative concentration of element was calculated by normalizing the individual element intensity to its atomic sensitive factor (ASF).

TEM imaging of nanoparticles and composites materials:

Before analysis, the composite mats were first ground into a fine powder using a mortar and pestle for 50 minutes. Samples were then prepared for TEM by ultramicrotomy with the mat materials sectioned as received, whereas the powder was dispersed throughout an epoxy embedding (TAAB) resin prior to sectioning. TEM imaging was performed on a FEI Tecnai Spirit operated at 120kV, with an AMT Nanosprint15 sCMOS camera. Diffraction data was acquired at a camera length of 0.54m, with a calibrated pixel size of 0.006231 nm⁻¹ per pixel. This value was revised by 2% to improve the fit of the maghemite diffraction rings, accounting for a systematic offset in the camera calibration.

Lead acetate paper for H₂S detection (control experiments)

A 0.5 g sample of 50-poly(S-*r*-canola) polymer was placed into two test tubes and 0.5 grams of elemental sulfur was placed into two separate test tubes. One lead acetate test strip (Precision Laboratories) was secured to the end of each of the test tubes using tape ensuring that any gas leaving the tube would come into contact with the strip. One of the two test tubes for each material was first wet with water before undergoing the test. The test tubes where then heated using a Bunsen burner until the sample underwent combustion. The samples were left to combust for 2-5 minutes ensuring that any gasses produced flowed over the strips attached to the tubes end. After this time, the samples were left to cool to room temperature and the strips were analysed:



Test strips (wet and dry) after heating poly(S-r-canola) polymer and elemental sulfur.

When the test strips were wet, they reacted to a greater extent and resulted in a more pronounced black color. For this reason, the test strips were soaked in water before use in the large-scale polymer synthesis to test for H_2S production. Burning elemental sulfur also resulted in some darkening of the test strips, especially when wet (see image above). This suggests that these strips also have some off-target reactivity to other reactive sulfur species which could be formed, such as gaseous elemental sulfur or SO₂. However, the most pronounced darkening of the strips was in the combustion of 50-poly(S-*r*-canola), which is consistent with production of H_2S (among other sulfur-containing gases) during polymer degradation.

Synthesis of 50-poly(S-r-canola) polymer and assessment of H₂S production

First, an overhead mechanical stirrer (Heidolph Hei-TOROUE 200) equipped with a stainlesssteel impeller (15 cm square blade) was secured on an H-frame stand. A stainless-steel reaction vessel (4.7 L, 20 cm diameter) was then placed on a hotplate. The impeller blade was placed several millimetres from the bottom of the vessel and the temperature probe was positioned towards the sides of the reaction vessel to ensure that it did not hit the impeller during the synthesis and was not touching the sides or bottom of the vessel. A funnel was also positioned next to but not touching the temperature probe again ensuring that it too was not in range of the impeller. Cable ties were then used to secure the reactor handles to the H-frame stand. The hotplate also holds the reaction vessel in place through magnetic force. Three stainless steel rods were secured onto a height-adjustable stand with tape and cable ties, in a way which allowed them to be placed over the reaction vessel without contacting the impellor, the temperature probe, or the funnel. Lead acetate strips, used for indicating the presence of H₂S, were attached to the rods over the reactor using paper clips. Three different brands of strips (1. Precision laboratories, 2. Cytiva Whatman and 3. Westlab) were used and arranged along each of the rods. Before the strips were arranged above the reaction vessel they were soaked in deionised water. The final setup is shown below:



Next 375.0 grams of canola oil was added to the reaction vessel. Separately 375.0 grams of elemental sulfur and 1750 grams of NaCl were weighed. The NaCl was ground into a fine powder before use in the experiment, to ensure it was free flowing upon addition to the reaction. The temperature of the reaction vessel containing the canola oil was set to 170 °C and the stirring was set to 90 rpm. After 6 minutes of heating, the canola oil reached 170 °C and the sulfur was then added into the reaction through the funnel over 4 minutes ensuring the

temperature remained above 160 °C. After addition of the sulfur, the NaCl was added slowly over 25 minutes through the funnel, again ensuring that the temperature never dropped below 160 °C. As more salt was added and the reaction time increased, the viscosity of the mixture also increased. After the NaCl addition was complete, the viscosity of the mixture continued to increase. The overhead stirrer's torque meter was monitored and when it registered 40 N•cm, the agitation was stopped and the reaction vessel was removed from the hot plate. The product solidified and was left to cool down to room temperature. A large metal spatula was used to break up the solid product in the vessel before it was transferred into a grinder to grind the particles up into smaller pieces. These salt and polymer particles where then washed with water three times and then air dried. The resulting polymer particles were then characterised by ¹H NMR, DSC, TGA, SEM/EDX, XRD, and FTIR.

During the reaction, the H_2S test strips were monitored and slowly darkened in colour over time (see figure below). The largest extent of blackening occurred during the addition of the elemental sulfur. The strips did still increase in darkness once NaCl addition began.



These results suggest that some reactive sulfur species (potentially H_2S or SO_2 or gaseous elemental sulfur) may have been formed on the addition of sulfur. For this reason, reactions of this scale must be carried out with suitable ventilation. However, the strips only darkened slightly, which means there is far less H_2S produced during polymer combustion (see page S4). These test strips have a limit of detection of approximately 5 ppm H_2S . This protocol, therefore, is sufficient to control the exothermic reaction, prevent polymer degradation, and minimise H_2S production.

50-poly(S-r-canola) characterisation

NMR, TGA, DSC, SEM, EDX, XRD, IR, and combustible analysis are provided below. These characterisation data are consistent with and complement data previously published for this polymer system.¹⁻⁵



¹H NMR (600 MHz, pyridine-D5). Note that the solvent breaks S-S bonds and this is therefore a destructive analytical technique for this sample. Key signals include the glycerol derived signals in the triglyceride (a, c, d), some unreacted alkene in the triglyceride (b), and the methyl groups of the triglyceride (h). Based on the relative integration of the alkene signal and the methyl groups, and comparison to the canola oil starting material, approximately 81% of the alkenes are consumed in the polymerization.¹



Thermogravimetric analysis (TGA). The first mass loss onset occurs at approximately 230 °C and corresponds to degradation of the sulfur domain of the product (polysulfide S-S bonds and elemental sulfur). A second degradation onset occurs at approximately 350 °C, which corresponds to the degradation of remaining organic matter. After heating to 800 °C, 12% of the mass remains.



Glass transition temperature by differential scanning calorimetry (DSC). A glass transition temperature for the sample was measured to be -26 °C. This is consistent with the soft, rubbery consistency of 50-poly(S-*r*-canola) at room temperature, when prepared by the synthesis described on pages S5-S6.

Unreacted elemental sulfur content (estimated by DSC): Initially 1.0 mg of elemental sulfur was placed in the aluminium crucible for DSC analysis. The crucible was placed in the DSC 800 dynamic scanning calorimeter and the temperature was set to hold at 30 °C for 2 minutes. The temperature was then raised to 150 °C at a rate of 10 °C / minute. Once it reached 150 °C the temperature was held for 2 minutes before the run was stopped. This process was then repeated for elemental sulfur masses of 2.0, 4.0, 6.0 and 8.0 mg. The endothermic peaks occurring between 110 °C and 130 °C where then integrated and their Δ H (J) values obtained. The values for Δ H where then plotted against the masses of sulfur to create a calibration curve. The free sulfur endotherm for a 10 mg sample of 50-poly(S-*r*-canola) was then integrated. Using this value and the calibration curve, the free sulfur content of the polymer was approximately 20 wt%.^{1,2}



Scanning electron microscopy and energy-dispersive X-ray spectroscopy of polymer surface. The elemental composition of the 50-poly(S-*r*-canola) contains a relatively uniform distribution of carbon, oxygen, and sulfur.



Powder X-ray diffraction. Diffraction patterns of 50-poly(S-*r*-canola) are consistent with the presence of some unreacted, crystalline S_8 .



Infrared spectroscopy. The infrared spectrum of 50-poly(S-*r*-canola) has signals at 2924 cm¹ (CH stretch) and 1741 cm⁻¹ (C=O stretch) arising from the triglyceride (canola oil) comonomer.

Sample ID	Weight (mg)	N%	С%	Η%	S%
50-poly(S-r-canola)	4.756	-	38.81	4.92	48.52
	5.125	-	38.33	5.07	49.76
Theoretical values	-	-	38.75	5.82	50

Combustible analysis for elemental composition. The expected sulfur content by mass was 50% based on the feed ratio of elemental sulfur in the reaction. The theoretical carbon and hydrogen content was based on an approximate structure of the canola oil triglyceride containing 2 units of oleic acid and 1 unit of linoleic acid per triglyceride monomer.² The results are in agreement with the expected value and good mass balance. Additionally these results are consistent with good atom economy and minimal loss of sulfur (through sublimation or H₂S or SO₂) during the polymerization.

Preparation of 50-poly(S-*r*-canola) / γ-Fe₂O₃ composite mats

1 gram of γ-Fe₂O₃ nanoparticles (< 50 nm, Merck) were added to a 50 mL centrifuge tube along with 6.5 grams of 50-poly(S-*r*-canola). The tube was then inverted multiple times to mix the iron nanoparticles and the polymer together. This mixture was then placed into the 10 × 10 cm aluminum mold between two sheets of PTFE paper. The mould was then placed into a S15 Devils press 10-ton hydraulic heated press that was pre-heated to 100 °C. Once the temperature of the system had equilibrated at 100 °C, the pressure was increased to 40 MPa. The pressure immediately starts to fall due to the moulding reducing the volume of the material. Once the pressure dropped and stabilised the pressure was increased back up to 40 MPa. After 10 minutes, the pressure was relieved, and the mould was removed from the press. The mould was opened and the resulting 50-poly(S-*r*-canola) / γ-Fe₂O₃ composite mat was removed from the PTFE paper:



This mat was shown to maintain its magnetic properties by demonstrating its affinity towards a permanent magnet:



Comparison of 50-poly(S-r-canola) / γ -Fe₂O₃ blend with different γ -Fe₂O₃ ratios

1.0 gram of γ -Fe₂O₃ nanoparticles (< 50 nm) was added to a 50 mL centrifuge tube along with 6.5 grams of 50-poly(S-*r*-canola). The tube was then inverted multiple times to mix the iron nanoparticles and the polymer together. This was repeated using 2.0 grams of γ -Fe₂O₃ nanoparticles. Both mats were contiguous mats that could be handled:



Preparation of composites with different ratios of γ -Fe₂O₃

To increase the nanoparticle content, the composite powder (1.0 gram of γ -Fe₂O₃, 6.0 grams of 50-poly(S-*r*-canola)) prepared above was added into a new 50 mL centrifuge tube. To this tube an extra 1.0 grams of γ -Fe₂O₃ nanoparticles was added and the mixture was shaken to ensure optimal surface coverage of γ -Fe₂O₃ nanoparticles on the polymers surface. This mixture was then placed into the 10 × 10 cm aluminium mould between two sheets of PTFE paper. The mould was then placed into the S15 Devils press 10-ton hydraulic heated press that was previously heated up to 100 °C. Once the temperature of the system had equilibrated at 100 °C, the pressure was increased to 40 MPa. The pressure immediately starts to fall due to compression reducing the volume of the material and therefore the pressure. Once the pressure stabilised it was increased back up to 40 MPa. This was repeated until the pressure was stabilised at 40 MPa. After 10 minutes, the pressure was relieved, and the mould was removed from the press. The mould was opened and the resulting 50-poly(S-*r*-canola) / γ -Fe₂O₃ composite mat was removed from the PTFE paper. The mat was then ground back up into a powder to form the magnetic composite powder shown below.



A) γ -Fe₂O₃ nanoparticles, B) 50-poly(S-*r*-canola) particles, C) Blend of A and B, D) Magnetic γ -Fe₂O₃ nanoparticles embedded in 50-poly(S-*r*-canola).

Preparation of composites with different ratios of γ-Fe₂O₃ (continued)

1.0 gram of 50-poly(S-r-canola) was added to 0.33 grams of γ -Fe₂O₃ nanoparticles and mixed to homogenize. The mixture was then placed into the 10×10 cm mould in between two sheets of PTFE. The lid was added to the mould and the entire system was placed into the heated press at 100 °C. Once the mould equilibrated at 100 °C the pressure was increased to 20 MPa gradually over 1 minute. After remaining at 20 MPa at for 1 minute the pressure was increased to 40 MPa. After remaining at 40 MPa for 1 minute, the pressure was increased to 60 MPa. The mould was left under 60 MPa pressure at 100 °C for 10 minutes. At this point the pressure was removed and the lid and top layer of PTFE sheeting was removed to reveal the mat formed inside the mould. It was noticed that the mat formed was not homogenous, and areas existed with very high nanoparticle to polymer ratios. The sample was broken up within the mould using a metal spatula and mixed briefly within the mould. The top sheet of PTFE was re-added along with the mould lid and the process of moulding at 60 MPa was repeated. After repeating this process 2 times a solid mat had formed with limited defects. The above process was repeated using 1.0, 3.0, and 9.0 grams of y-Fe₂O₃ nanoparticles to achieve composite mats with 25, 50, 75 and 90 wt% γ-Fe₂O₃ nanoparticles content. Above 75 wt% γ-Fe₂O₃ content, the mat was not contiguous and formed cracks and was fragile.

Iron(III) oxide nanoparticles Poly(S-*r*-canola) particles 😯 Magnetic composite powder



Diagram describing the process used to make composites with uniformly distributed nanoparticles.



Images of composites formed by reactive compression moulding of mixtures of 50-poly(S-*r*-canola) and γ -Fe₂O₃ nanoparticles.

SEM / EDX

 γ -Fe₂O₃ nanoparticles were analysed by SEM as received from Merck



SEM / EDX

A composite mat was prepared as described previously at 25 wt% γ -Fe₂O₃ nanoparticles and 75 wt% of the 50-poly(S-*r*-canola) polymer binder. A cross-section was analysed by SEM and EDX to reveal a relatively uniform distribution of iron particles in the polymer matrix.



STA analysis of composites

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a 449 F5 Jupiter simultaneous thermal analyser. A sample size between 4-5 mg was used in each run. The furnace was purged at 20 mL/min with nitrogen and equilibrated for 1 minute at 30 °C before each run. Heating was carried out up to 600 °C using a 20 °C/min heating rate. The temperature was held isothermally at 600 °C at the end of each experiment to oxidize remaining organic matter. The results are shown below. The final mass was consistent with the mass of the inorganic iron content of the composite.



DSC (left) and TGA (right) plots for composites with varying γ -Fe₂O₃ nanoparticle (FeNP) contents.

X-ray photoelectron spectroscopy (XPS) of magnetic responsive composites

The composites were prepared in powder form and mounted on a sample holder. Highresolution scans of C, O, S and Fe of the samples were recorded and fitted. The spectra of S and the relative intensity of S species are shown in the figure below.



A. Fitting of S 2p spectra of samples B. Relative intensity of difference S species observed

The fitting of S2p3/2 results in three distinguishable components. The main species can be fitted at 164.2 ± 0.15 eV, which is identified as C-S species from canola oil polymer.¹ The one fitted at 162.8 ± 0.15 eV only occurs in polymer substrate. This peak should also include any

S-S bond present from the polysulfide groups in the polymer.⁸ The lower binding energy S species located at the shoulder of a main peak may be due to the fitting background interference. The third peak fitted at $168.5 \pm 0.15 \text{ eV}^{9,10}$ may be due to a high oxidation form of sulfur such as sulfate (SO_{x+}), which may result from thermal degration of the polymer. However, this interpretation should be approached with caution as these peaks also overlap with the signals iron oxides observed in the pure nanoparticles.¹¹

The spectra of C and Fe are shown in the figure below. It should be noted the calibration of C-C sp3 to 285.0 eV was referred to the fitting of C1s.^{12,13} While the S2p3/2 of S species assigned to polymer C-S can be fitted at 164.2 ± 0.15 eV.^{1,14}



A. Fitting of C 1s spectra of samples; B. Fitting of Fe 2p3/2 spectra of samples

XRD analysis of magnetic responsive composite powders

Composite mats were ground into fine powder for analysis. The 100 wt% γ -Fe₂O₃ nanoparticles after moulding sample was prepared by hot-pressing 100 wt% γ -Fe₂O₃ nanoparticles according to the sample preparation process for the composite (this processing was done as a control). The resulting γ -Fe₂O₃ layer was removed from the PTFE paper and ground into a powder for XRD analysis. The results are shown in the figure below.



XRD plots for 0-90 wt% γ -Fe₂O₃ composite powders and 100 wt% γ -Fe₂O₃ nanoparticles before and after moulding, indicating there is no change in the diffraction after hot-pressing.

TEM Analysis

Before analysis, the composite mats were first ground into a fine powder using a mortar and pestle for 50 minutes. Samples were then prepared for TEM by ultramicrotomy with the mat materials sectioned as received, whereas the powder was dispersed throughout an epoxy embedding (TAAB) resin prior to sectioning. TEM imaging was performed on a FEI Tecnai Spirit operated at 120kV, with an AMT Nanosprint15 sCMOS camera. Diffraction data was acquired at a camera length of 0.54 m, with a calibrated pixel size of 0.006231 nm⁻¹ per pixel. This value was revised by 2% to improve the fit of the maghemite diffraction rings, accounting for a systematic offset in the camera calibration.



TEM images of 100 wt% γ -Fe₂O₃ nanoparticles (as received, Merck).

The nanoparticles have a broad size distribution, varying from approximately 5-250 nm and show clear diffraction rings corresponding to the gamma γ -Fe₂O₃ crystal structure. Some of these nanoparticles are therefore larger than the <50 nm range indicated by the supplier. Next the nanoparticles within the composite materials were analysed. TEM analysis of the composites clearly shows the distribution of the denser γ -Fe₂O₃ particles dispersed throughout the polymer.



TEM images of magnetic responsive composite powder (25 wt% $\gamma\text{-}Fe_2O_3)$



TEM images of magnetic responsive composite mat sample (25 wt% γ -Fe₂O₃)



TEM images of the magnetic responsive composite powder (75 wt% γ -Fe₂O₃)



TEM images of the magnetic responsive composite mat sample (75 wt% γ -Fe₂O₃).

As shown in the figures above, the nanoparticles are clearly observable in all composite samples and appear not to have aggregated into larger particles during the formation of the composite. This offers further evidence that the nanoparticles are simply being encapsulated by the polymer matrix and do not appear to be reacting.

The figure below shows that there is a reasonable distribution of nanoparticles throughout the polymer however there are some regions of higher iron particle density. This distribution is sufficient for the magnetic responsiveness required for the applications examined in this study and for excellent mass recovery of the polymer via magnetic retrieval.



TEM images of the 25 wt% composite material (left) and the 75 wt% composite material (right).

Highlighted in the figure below, TEM / EDS analysis revealed further evidence that the composites contain regions which have a distribution that varies from dense regions of closely packed nanoparticles to areas with the nanoparticles dispersed over the poly(S-*r*-canola) polymers surface. Again, this distribution is still sufficient for the magnetic responsiveness required for the applications in this study.



A)TEM images of 75 wt% γ -Fe₂O₃ composite powder highlighting areas of high sulfur (left) and iron oxide (right) content determined through EDS. B) TEM image of 75% composite used for analysis of EDS diffraction pattern (right).

From the figure above (A), it appears as if there are regions of high sulfur content and regions of high iron content. The sulfur region contains both sulfur polymer and iron oxide nanoparticles whilst the iron region contains mainly iron oxide. This suggests that there are regions of the 70 wt% γ -Fe₂O₃ composite which are well dispersed and others which consist almost entirely of γ -Fe₂O₃ nanoparticles without polymer. This is consistent with the observation that this is the upper limit of the iron amount and there is not enough polymer to hold such a composition together in a solid mat. In part B in the figure above, the diffraction patterns (right) produced form the composite sample (left). These patterns showed very bright bands which correspond to the maghemite (γ -Fe₂O₃) crystal structure as well as some weaker bands that may be from other crystal phases of irons oxide, such as hematite and magnetite.

Direct addition of γ-Fe₂O₃ particles during 50-poly(S-*r*-canola) polymer synthesis

Sulfur (technical grade, 10.0 g) was added to a 250 mL round bottom flask and then heated to 120 °C to melt the sulfur over 10 minutes, before heating further to 180 °C. The reaction was stirred using an overhead stirrer. Canola oil (10.0 g) was then added dropwise over 5 minutes. Two separate phases where present upon addition of the canola oil. Next 6.67 g of γ -Fe₂O₃ was added to the mixture over 2 minutes (to prepare the composite containing 25 wt% γ -Fe₂O₃). Upon stirring, the iron nanoparticles were present in both phases, but most of the nanoparticles were confined in the molten sulfur. The sulfur layer seemed to become more viscous upon combination with the nanoparticles. The canola oil layer remained liquid and not as viscous. 50 minutes after the addition of the canola oil the reaction appeared to become one uniform viscosity, which is far longer than if the polymer is prepared without the added γ -Fe₂O₃ particles. Within 10 minutes of forming one phase (~60 minutes total reaction time) the reaction solidified to form a black rubber. This material was visibly darker than the 25 wt% composite prepared using the hot-press method:



Magnetic responsive composite (25 wt% γ -Fe₂O₃) prepared by direct addition of iron nanoparticles to the polymerization



Magnetic responsive composite (25 wt% γ -Fe₂O₃) by hot-pressing preformed 50-poly(S-*r*-canola) with the iron nanoparticles

The composite formed by addition of γ -Fe₂O₃ to the polymerization of sulfur and canola oil was still responsive to a magnet:



The polymer component of the composite made by direct addition of γ -Fe₂O₃ to the polymerization reaction was similar to 50-poly(S-*r*-canola), as determined by IR and EDX:



Above: the IR spectrum of the composite made by the direct addition of γ -Fe₂O₃ to the polymerization is the same as 50-poly(S-*r*-canola).



Above: EDX of the composite made by the direct addition of γ -Fe₂O₃ to the polymerization.

¹H NMR analysis in pyridine-D5 indicated the hot pressing method consumed more alkenes than in the composite preparation in which the γ -Fe₂O₃ particles are added during the polymerization. This indicates the hot-pressing can result in continued reaction (cleavage of S-S bonds and addition of thiyl radicals to unreacted alkenes, for instance). Additionally, the undissolved iron particles in the NMR sample of the composite prepared by the hot-pressing method are red. The undissolved iron particles in the NMR sample of the composite prepared by the direct addition of the γ -Fe₂O₃ during the polymerization are black:



Above: The direct addition of the γ -Fe₂O₃ particles to the polymerization results in the formation of a black product. When dissolving (and sonicating) the polymer in pyridine-D5 for NMR analysis, the undissolved solid is red for the composite made by hot-pressing (compression), while the undissolved solid is black for the composite made by direct addition of the γ -Fe₂O₃ particles during the polymerization. Below: the alkene region (highlighted) indicates greater alkene consumption when the composite is prepared by hot-pressing (compression).



Even though the recovered iron was black when the iron particles were added directly to the polymerization, powder X-ray diffraction data was no different than for when the magnetic responsive composite was prepared by hot-pressing:



Demonstration of magnetic retrieval of composite powder in water

1 gram of composite powder (25 wt% γ -Fe₂O₃) was added to a 50 mL centrifuge tube along with 30 mL of D.I. water. The lid was placed onto the tube and the entire tube was placed on a rotary mixer for 5 minutes. After 5 minutes had passed the tube was removed from the mixer and a magnet was used to draw the polysulfide to the bottom of the flask and the remaining solution was decanted off. The process was complete within 3 seconds.



This process was repeated in a slightly different format to clearly illustrate removal from water: To a 50 mL centrifuge tube, 0.5 gram of the composite material (25 wt% γ -Fe₂O₃) was added along with 40 mL of deionised water. The solution was mixed into a vortex to ensure the composite was fully suspended within the water. Next a permanent magnet was placed directly next to the solution to attract the composite to the magnet as the water settled to the bottom of the tube. The process was complete within 3 seconds:



Magnetic filtration of composite material from fine tailings in HgCl₂ doped solution

3.0 grams of mine tailings was added 3×50 mL centrifuge tubes. Next, 1 gram of the 50poly(S-*r*-canola) / γ-Fe₂O₃ nanoparticles composite was added, followed by 20 mL of aqueous HgCl₂ solution (~5 ppm). The mixture was mixed on an end-over-end mixer at 25 rpm for 24 hours. After 24 hours the mixing was stopped. Then, a magnet was used to draw the composite to the sides of the centrifuge tube and the remaining solution/tailings was decanted off into a clean 50 mL centrifuge tube. A magnet was applied to wall of the new tube and no particles were observed to stick to the wall suggesting that no magnetic composite was in this mixture. This mixture was then filtered, and the remaining solution was transferred into a 20 mL glass vial for analysis. The composite remaining in the original tube had 50 mL of clean DI water added and the new mixture was mixed thoroughly. The magnet was then reapplied, and the composite was drawn to the wall. The remaining sand was again decanted off with the water leaving only the composite remaining. The composite was left in the fume hood to dry overnight. A magnet was again used to remove the dried composite from any contaminant sand. Approximately 1 g of the magnetic responsive powder was recovered in all three runs. The purified water was then analysed by CVAA spectroscopy, indicating a mercury concentration of 6.7 ppb. The original concentration of mercury in the water was 5000 ppb.



Images demonstrating the magnetic filtration and separation of the composite powder from a tailings / water slurry.



The dried composite powder was further separated from contaminant sand using a magnet in a plastic bag.

Recovery of iron oxide from composite after use as mercury sorbent

Initially a HgCl₂ solution was prepared by adding 1.0 g of HgCl₂ into 200 mL of deionised water. To a 250 mL beaker, 200 mL of HgCl₂ solution (2.5 g/L) was added along with 10 grams of the magnetic responsive composite (25 wt% γ -Fe₂O₃). The mixture was stirred for 2 hours, after which time the composite was retrieved using a magnet and washed three times with water. The recovered composited was then left to dry overnight in the fume hood. A small portion of this sample was then analysed using SEM/EDX, which confirmed mercury was bound to the surface of the composite:



6.00 grams of the remaining Hg contaminated composite material was then added to a crucible. The crucible was then placed in a furnace which was set to heat up at a rate 5 °C / min until it reached 1200 °C. This process has previously been shown to convert bound mercury to mercury metal, followed by volatilization. (For larger samples, a mercury scrubber and mercury recovery unit is required for this process). The temperature was then held at 1200 °C for 1 hour before the system was cooled back down to room temperature. The resulting black solid was 24% of the mass of the starting composite (25% was expected, which corresponds to a 96% recovery of the iron oxide). An image of the recovered iron oxide is shown below:



S30

SEM and EDX analysis of the recovered material was consistent with iron oxide. No mercury and no polymer or carbon was detected:



XPS analysis was also consistent with recovered iron oxide: Fe 2p3/2 Fitting



XRD analysis of the recovered iron oxide indicated that it formed α -Fe₂O₃ in the furnace. Hematite still retains magnetic properties, so it can still be used in the preparation of the magnetic-responsive composite. However, the phase change in the Fe₂O₃ crystal from γ -Fe₂O₃ (orange XRD pattern) to α -Fe₂O₃ (blue XRD pattern) in this process should be noted:



Ternary composite preparation and mechanical testing

To test the mechanical properties of the composite sheets containing 50-poly(S-*r*-canola), γ -Fe₂O₃ and polyvinylchloride (PVC) shavings, four mats were produced. A mat containing only 50-poly(S-*r*-canola) was first prepared as a control. Three composite mats were prepared with 50-poly(S-*r*-canola) and the additives. One composite contained γ -Fe₂O₃, one contained PVC and another had both γ -Fe₂O₃ and PVC additives. All compositions were made in an 88 mm by 40 mm aluminium mold and contained the same mass of polymer (10 g). The methods to prepare these mats differed slightly for each composite, as noted below:

The 50-poly(S-*r*-canola) mat was prepared by adding 10 g of the polymer to an 88 mm \times 40 mm aluminium mold between two sheets of PTFE paper. The mould was then placed into a S 15 Devils press 10-ton hydraulic press which was pre-heated to 100 °C. The press was left for approximately 5 minutes to equilibrate at 100 °C. The pressure was then slowly increased to 40 MPa and left for 10 minutes. The mould was then removed from the press, allowed to cool before it was opened, and the polymer mat was extracted. This mat had a mass of 7.8 g and a thickness of 1.73 mm.

The 50-poly(S-*r*-canola) / γ -Fe₂O₃ composite mat was prepared using the method described earlier but slightly modified to create thicker mats for testing the mechanical properties. The composite had a ratio of 75% polymer and 25% γ -Fe₂O₃ by mass. 3.33 grams of γ -Fe₂O₃ was added to 10 g of 50-poly(S-*r*-canola) and thoroughly mixed in a plastic container. This mixture was then added to an 88 mm × 40 mm aluminium mold between two sheets of PTFE paper. This was then compressed using the same procedure as the control. After this, the composite was ground back into a powder and compressed again using the same method. This process was repeated a total of three times to ensure a homogenous mat. After this process, the mat had a mass of 8.32 g and a thickness of 1.81 mm.

The 50-poly(S-*r*-canola)/PVC composite mat was prepared by mixing 10 g of the polymer with 4.43 g of PVC in a plastic container. This ratio was used as it is the same as what was used in the recycling experiment. This mixture was then added to an 88 mm \times 40 mm aluminium mold between two sheets of PTFE paper and compressed using the same procedure as the control. This mat had a mass of 11.17 g and a thickness of 2.35 mm.

The composite mat containing 50-poly(S-*r*-canola), γ -Fe₂O₃ and PVC was prepared by grinding up a freshly made 50-poly(S-*r*-canola)/ γ -Fe₂O₃ mat made by the method described above. 13.3 grams of this powdered composite was mixed with 4.43 grams of powdered PVC in a plastic container. This corresponds to a ratio of 75% 50-poly(S-*r*-canola) / γ -Fe₂O₃ composite and 25% PVC by mass. This mixture was then added to an 88 mm × 40 mm aluminium mold between two sheets of PTFE paper and compressed using the same procedure as the control. This mat had a mass of 14.03 grams and a thickness of 2.72 mm.

Images of all four specimens are shown on the next page.



The polymer composites were cut into the appropriate shapes for mechanical testing using a sharp scalpel. Each composite mat was cut into three 10 mm \times 10 mm square disks for compression testing, three 10 mm \times 30 mm rectangular prisms for tensile testing and three 10 mm \times 58 mm rectangular prisms for 3-point bending tests. All composites were tested in triplicate using a TA Q800 dynamic mechanical analyser. For compression and tensile testing, a force ramp rate of 3 N/min was used with a maximum of 18 N. The 3-point bending clamp was 49.4 mm wide and a force ramp rate of 0.2 N/min was used. All polymers were tested at room temperature.

The compressive or tensile stress (σ) in MPa was calculated by dividing the applied force (F) in N by the cross-sectional area of the samples (A) in mm². The strain (ϵ) was calculated by the change in length (dL) divided by the initial length (L₀) in mm. The Young's modulus (E) in Mpa was then calculated by the slope of the stress against strain plot:

$$\sigma = \frac{F}{A}$$
 $\varepsilon = \frac{dL}{L_0}$ $E = \frac{\sigma}{\varepsilon}$

The Flexural modulus was calculated using the slope of the force (F) in N against deflection (d) in mm plot of the rectangular samples in the 3-point bending test. The slope was multiplied cube of the length between the supports (L) in mm and divided by four times the product of the width (w) in mm and the cube of the height (h) in mm. This can be seen from the following equation:

$$E_{flex} = \frac{L^3 F}{4wh^3 d}$$

The composite mats with γ -Fe₂O₃ possessed a greater tensile modulus than those without. However, when PVC was added, the tensile modulus decreased. Most of the elongation of the composites likely occurs at the 50-poly(S-r-canola) portion as the PVC is notably less flexible. The PVC likely contributes to an increase in volume without contributing to the tensile modulus, resulting in a decreased value for these composites. This trend is reversed in the compression tests as the samples containing PVC had a greater compression modulus. This is likely because the effect of the inflexible PVC particles is increased as the sample is compressed due to a decrease in the average distance between particles. The 3-point bending test showed the greatest difference between samples. The samples with γ -Fe₂O₃ contained a higher flexural modulus than those without. However, the greatest change in flexural modulus came from the addition of PVC to the composite. These samples also showed different failure characteristics as they would fail at a decreased deflection but a much greater force. The samples without PVC did not rupture but instead reached the maximum deflection of the instrument at a low force while the composites with PVC would fail at the centre at a deflection between 3 and 5 mm. This indicates that the addition of the PVC particles creates a more rigid but brittle composite. The composite containing both γ -Fe₂O₃ and PVC failed at a much greater force than the composite containing only PVC with an average force at failure of 1.08 N and 0.493 N respectively. This may be due to the increased tensile strength of the composites with γ -Fe₂O₃ as failure occurs due to tension in these tests. A summary of the samples and mechanical testing outcomes is shown below:



Ternary composite preparation and recycling

4 grams of 25 wt% magnetic composite powder was added to 1 gram of waste PVC shavings in a plastic container. This mixture was inverted to mix and then added to a 10×10 cm steel mould in between two sheets of PTFE. The mould was added to the heated press, which was pre-heated to 100 °C. Once the temperature had equilibrated at 100 °C the pressure on the press was increased up until 40 MPa. The pressure was maintained at 40 MPa for 20 minutes. After 20 minutes the pressure was released, and the mould was removed from the press. The resulting composite mat was removed from the mould and separated from the PTFE sheets.



50-poly(S-*r*-canola) / Fe_2O_3 / PVC blend before (left) and after (right) being moulded into a composite mat.

This mat was then ground back up into a powder. Once ground into a powder, physical magnetic separation was performed to remove any magnetic composite from any non-magnetic filler materials (i.e. waste PVC shavings). The separated filler material was weighed and stored. The separated magnetic composite was ground back up into a powder and magnetic separation was performed again and the separated composite and filler were weighed. This process repeated until all the filler material had been recovered from the composite. This took a total of 10 mill and separate cycles to achieve full separation and mass balance.



Images showing the process of magnetically separating the composite from other components in a solid-solid mixture.

Microwave heating

0.75 grams of the magnetic responsive powder (25 wt% γ -Fe₂O₃) was placed on a 10 × 10 cm sheet of PTFE paper. An IR thermometer was used to measure the temperature. The thermometer was scanned over the surface of the material and the highest temperature observed during the scan was recorded as the temperature. This was done before irradiation to establish the initial room temperature of the material. This was repeated three times for triplicate measurements. A standard household microwave (1100W) was used to irradiate the samples. The microwave tray in the household microwave was observed to heat up under microwave irradiation introducing the possibility of heat transfer from the tray to the sample. The tray was therefore removed from the microwave to eliminate other potential heat sources. The sample was then placed in the microwave and irradiated for 10 seconds. At ten seconds the door was opened, the sample was quickly moved onto the benchtop and the temperature was recorded using the IR thermometer. Again, the thermometer was scanned over the surface of the sample and the highest value was recorded. Once the sample had cooled back to room temperature this was repeated two more times to get triplicate values for 10 seconds irradiation time. This process was repeated, in triplicate, for irradiation times of 20, 30, 40 seconds. This process was repeated using 50-poly(S-*r*-canola) powder, γ -Fe₂O₃ nanoparticles and PTFE sheet as controls. The samples and temperature change profile are shown below.



A) 0.1 grams of γ -Fe₂O₃ nanoparticles **B)** 0.65 grams of 50-poly(S-*r*-canola) polysulfide, **C)** 0.75 grams of 50-poly(S-*r*-canola) / γ -Fe₂O₃ composite material.



For samples irradiated for 50 seconds, clear signs of degradation were observed. This is consistent with TGA that shows decomposition onset at >200 °C



1 cm

1 cm

FLIR imaging of composite after 20 seconds of microwave irradiation

0.75 grams of composite material was placed onto 10×10 cm PTFE sheet and placed into the microwave. The sample was heated for 20 seconds. After the radiation the sample was immediately removed from the microwave and placed directly on the bench and imaged using the FLIR camera. The Images were taken every 10 seconds for 3 minutes. This was repeated with 0.75 grams of composite material in a thin mat (~1mm thick), a composite disk (~13 mm diameter, ~ 0.6 cm thick) and the 50-poly(S-*r*-canola) / γ -Fe₂O₃ nanoparticle mixture used to prepare the composite:





FLIR thermal imaging of blend of 50-poly(S-*r*-canola) and γ -Fe₂O₃ nanoparticles and after microwave irradiation for 20 seconds. The exposed γ -Fe₂O₃ nanoparticles heat rapidly.



FLIR thermal imaging of magnetic responsive powder (first moulded and then milled to powder). The composite (rather than the mixture before moulding) does not heat as rapidly as the exposed γ -Fe₂O₃ nanoparticles.



FLIR thermal imaging of composite disk before and after microwave irradiation for 20 seconds.

Difference in temperature after 5 seconds of microwave irradiation

 0.5×0.5 mm squares of composites materials consisting of 10, 25, 50, 75 and 90 wt% γ -Fe₂O₃ nanoparticle content were placed onto a 5 × 5 cm sheet of PTFE and their initial temperatures were recorded by taking an image of the samples using the FLIR thermal imaging camera. The samples were then placed in the microwave. The samples were heated for 5 seconds, after which time they were instantly imaged with the FLIR thermal imaging camera. Images of the samples were recorded every 10 seconds over 1 minute and are shown in the figure below.



FLIR images of composite mats with varying iron content after 5 seconds of microwave irradiation.

Comparison of heating rates against y-Fe₂O₃ nanoparticles

 0.5×0.5 mm squares of composites materials consisting of 10, 25, 50, 75 and 90 wt% γ -Fe₂O₃ nanoparticle content were placed onto a 10×10 cm sheet of PTFE and their initial temperatures were recorded by taking an image of the samples using the FLIR thermal imaging camera. The samples were then placed in the microwave. The samples were heated for 5, 10, 15, 20, 25 and 30 second time periods. To avoid degradation once a sample had reached 150 °C further irradiation was stopped. The temperature was recorded using the FLIR thermal imaging camera. This process was repeated three times to gain triplicates for each sample and each irradiation time.



Plot of temperature against microwave irradiation time (s) for each composite.

Linear trendlines were fitted to each of these data sets



Fe Content (wt%)	Rate (°C/s)
25	6
50	14
75	23
90	27

The slope of each of these points is equivalent to the heating rate under microwave irradiation.

Microwave induced reactive compression moulding

Microwave heating polypropylene syringe control

A 5 mL polypropylene syringe was placed into the household microwave and its initial temperature was recorded using a handheld IR thermometer. The polypropylene syringe was then irradiated for 10 seconds, after which the door was immediately opened, and the temperature was recorded using the handheld IR thermometer. This was repeated three times for triplicate measurements. This process was then repeated for irradiation times of 20 and 30 seconds.

Initial temperature = $21 \degree C$

No significant change in temperature occurred.

Reactive compression moulding of composite in microwave

The magnetic composite powder (2.5 grams total, 25 wt% γ -Fe₂O₃ and 75 wt% 50-poly(S-*r*-canola)) was placed into a 5 mL polypropylene syringe. The plunger was then inserted, and pressure was applied to the composite for 1 minute, compacting it and forcing the particles into contact. The syringe containing the compressed composite was then inserted into the microwave and the sample was irradiated for ~14 s. Directly after this, the sample was removed from the microwave and compression was re-applied to the plunger to re-compress the composite. This was done until the sample had cooled back down to 30 °C, determined using IR thermometer. The syringe was then placed back into the microwave and the sample was irradiated for an additional 3 × 14 s to ensure consolidation into a solid composite cylinder. After the final irradiation cycle, the composite was removed from the syringe.



Syringe containing unmoulded composite powder (left) and the resulting moulded composite cylinder (right).



A) Image demonstrating the ability to pick up the magnetic composite cylinder using a magnet,
B) Image of composite cylinder after an additional 20 seconds of heating shows deformation due to overheating and polymer decomposition. Care must be taken to not exceed 200 °C.

Moulding composite into cylinders and disks using reactive compression moulding in the microwave

All samples prepared using the protocol describe above. First 0.8 grams of the magnetic responsive composite powder (25 wt% γ -Fe₂O₃ and 75 wt% 50-poly(S-*r*-canola)) were added into a 20 mL polypropylene syringe. The plunger was inserted, and the composite was compressed within the syringe by applying constant pressure to the plunger. Pressure was applied for 1 minute before placing the entire syringe into an empty household microwave (1100W) and performing the above protocol. This process was repeated using a syringe with a smaller radius to achieve disks of different radius. This process was repeated in the 5 mL and 10 mL syringes using 3.2 grams of 25 wt% composite to form composite cylinders.



Syringe with composite within before moulding into disk.



Images showing the composite disks made from the magnetic composite using reactive compression moulding in the microwave.

Preparation of magnetic composite cylinder for solenoid valve component

2.0 grams of magnetic responsive composite powder (75 wt% γ -Fe₂O₃ and 25 wt% 50-poly(S*r*-canola)) was placed into a 3 mL syringe and the compressed by pushing the syringe closed. The entire syringe was then placed into the microwave and irradiated for 6 seconds in the microwave. The whole system was left to cool back to room temperature while applying constant pressure on the sample by pushing the plunger in. Once cooled back down to room temperature the system was placed back into the microwave and irradiated for a further 6 seconds followed by applying pressure and allowing it to cool back to room temperature. This was repeated 3 more times for a total of 5 x 6 second irradiation / cooldown cycles. Once the system had returned to room temperature the plunger was draw out pulling the formed cylinder back down the syringe. The end of the syringe was cut off using a scalpel and the resulting cylinder was pushed through the syringe and out of the end. The resulting cylinder stored in an oven at 100 °C for 2 additional hours to help further fuse the composite together. Note that the microwave curing step was a precaution to help further improve consolidation.

Construction of magnetic solenoid valve

The valve body was taken apart and the original operator was removed. A small steel spring was added to the top of the composite cylinder to ensure that the cylinder remained closed when the solenoid was not on. The cylinder was placed inside a plastic cylinder (radius = 1.0 cm, thickness = 0.2 cm) before being placed into the solenoid coil. This was to ensure that the composite cylinder fit tightly, and no leaks were possible.



Testing the use of the magnetic solenoid valve with magnetic composite component

50 mL of FeCl₃ solution was added to a 500 mL dropping funnel. Plastic tubing was used to connect the outlet of the dropping funnel with the inlet of the solenoid valve. Plastic tubing was also inserted into the outlet of the solenoid valve. The valve was held up by a retort stand and the pressure on the system was altered by changing the height of the dropping funnel with respect to the valve. The valve was positioned so that the liquid would flow through the valve vertically and a beaker was placed below the valve to catch the running liquid. The working solenoid valve with the magnetic composite component installed is shown below.



Images showing the working solenoid valve with magnetic composite replacing the operator inside it.

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