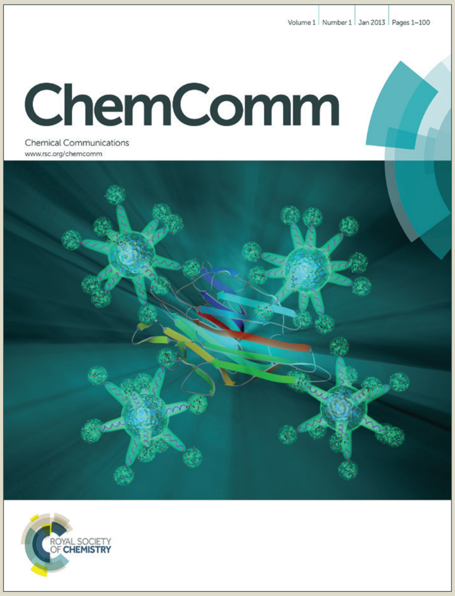

Nanoparticle-sulphur “inverse vulcanisation” polymer composites†

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Composites of sulphur polymers with nanoparticles such as PbS, with tunable optical properties are reported. A hydrothermal route incorporating pre-formed nanoparticles was used, and their physical and chemical properties evaluated by transmission and scanning electron microscopy, thermogravimetric and elemental analyses. These polymers are easily synthesised from an industrial waste material, elemental sulphur, can be cast into virtually any form and as such represent a new class of materials designed for a *responsible energy future*.

Sustainable chemical processes and those using waste materials provide alternate routes to a more environmentally benign economy of chemical utilisation. Sulphur is a promising alternative feedstock to carbon for polymeric materials and is a by-product from hydrodesulphurisation; a crucial step in the petroleum refining process. Large slag heaps of elemental sulphur residues can be found at petroleum refineries, especially when oil from sour fields is used, such as the sulphur rich oil sands of Athabasca, Canada (Fig. 1a). To date the utilisation of this waste is limited to sulphuric acid.[1]

In 2013, Pyun *et al.* showed that utilising elemental sulphur cross-linked with a divinylic species, 1,3-diisopropenylbenzene (DIB), a rubber industry feedstock, can create a thermosetting polymer, a process they dubbed inverse vulcanisation.[2,3] A deep red colour was observed on the addition of the DIB to molten sulphur at 185 °C. On further heating the materials set due to the divinylic groups of the DIB reacting with the radical polymeric sulphur chain ends, forming the final polymer.[4,5]

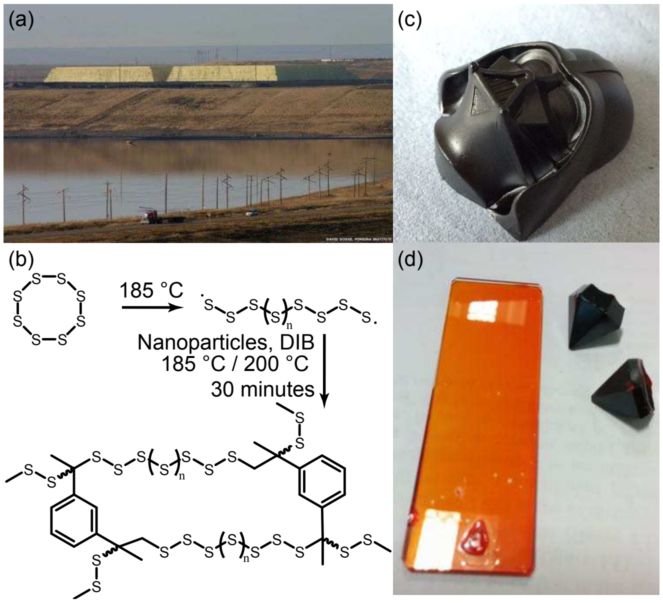

Fig. 1 (a) Sulphur wastes at Athabasca, Canada. Image used with permission: David Dodge, The Pembina Institute - www.pembina.org, (b) Scheme for formation of crosslinked polymer. (c) Moulded polymer containing Fe_3O_4 nanoparticles, (d) Raw polymer (no nanoparticles) in film and moulded forms.

The DIB-sulphur polymer may be useful for the incorporation of nanomaterials, and subsequent processing and moulding techniques multiply the potential uses of such composites.[6] The combination of new polymers with nanomaterials has potential to produce multi-functional optical materials for lenses and filters, or durable composites for structural applications.[7] In this paper, we describe a facile method for the incorporation of different types of nanoparticles into a sulphur polymer matrix, and demonstrate its malleability and useful optical properties.

Elemental sulphur has many allotropes, but the common yellow powder mainly comprises eight-membered S_8 rings. On heating, yellow sulphur melts at 120-124 °C,[8,9] before the critical temperature (the so-called λ-transition) of $\sim$159 °C at which the specific heat capacity, density, thermal expansion

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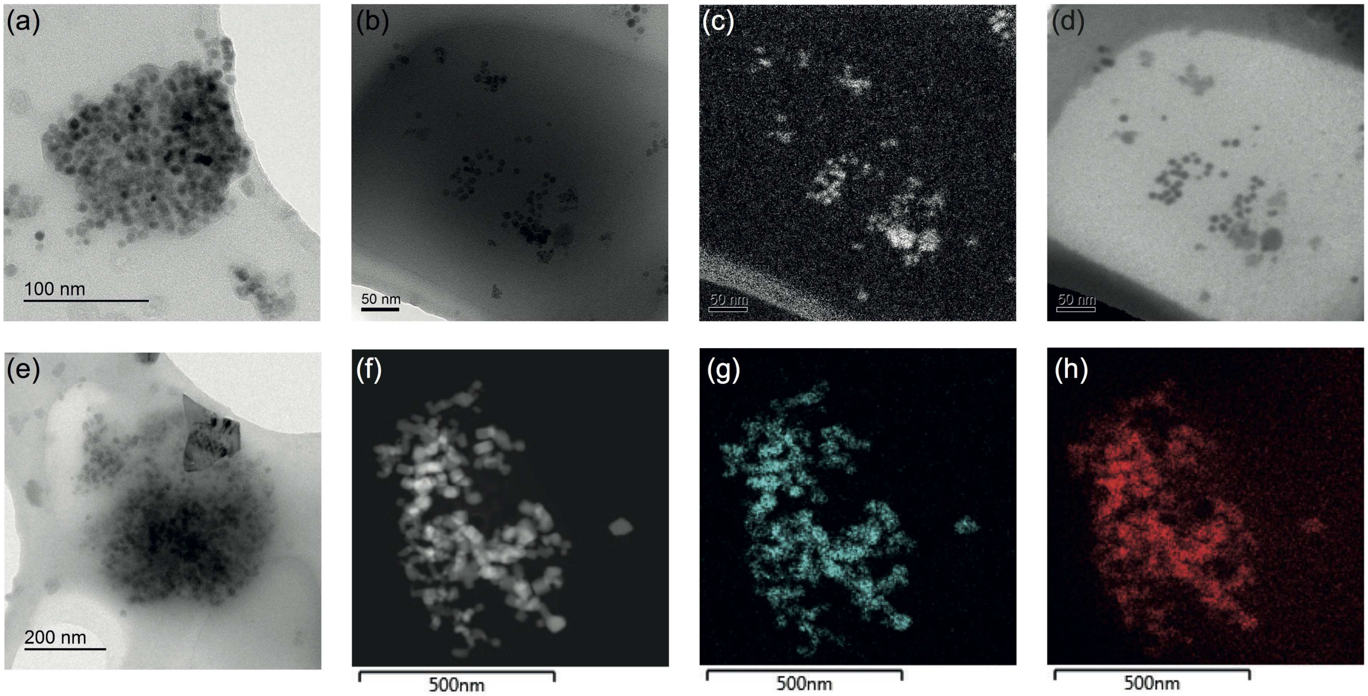

Fig. 2 a) Au nanoparticle-sulphur polymer composite, b) zero-loss TEM micrograph of Fe_3O_4 nanoparticle-sulphur polymer composite, c) EELS iron map of the Fe_3O_4 nanoparticle-sulphur polymer composite, showing iron glowing white, d) EELS sulphur map with sulphur glowing white, e) CoO nanoparticle-sulphur polymer composite, f) HAADF-STEM image of the PbS nanoparticle-sulphur polymer composite, g) Pb EDS mapping of f) and h) S EDS mapping of f) showing high concentrations of sulphur in the PbS nanoparticles and diffuse sulphur throughout.

and viscosity all alter dramatically. The changes are due to the ring opening of the S_8 species, forming long-chain oligomeric components with radical end groups.[2] A darkening in colour is also observed on heating, held to be due to organic impurities within the sulphur.[8]

Full details of the sulphur polymer synthesis and composite synthesis are given in the ESI(†), but briefly, 2 g (62.4 mmol) of elemental sulphur was heated with vigorous stirring to 185 °C in an oil bath at which point 50 wt. % of DIB (2.16 ml, 12.6 mmol) was injected rapidly. In order to incorporate nanoparticles ∼0.1 g of hydrophobically coated nanoparticles were dispersed in the required amount of DIB before addition. The mixture was then heated for 2-3 minutes before pouring into a mould. This process is summarised in Fig. 1b. Thin films were synthesised by drop-casting a small amount (∼1 mL) of the molten mixture onto a cold microscope slide, adding a second slide as a cover-slip before curing at 200 °C for 30 minutes. Thin films were then analysed using UV/vis absorption spectroscopy (Fig. 3).

The sulphur polymer itself is a ruby-red glassy material with rheological properties that depend on the amount of DIB in the synthesis, raising the glass transition temperature (T_g).[2] The composition of the polymer was evaluated using elemental analysis and XPS. Elemental analysis on a 50 wt.% DIB-sulphur polymer sample fitted with the postulated structure (Fig. 1c),[2] but any discrepancies were attributed to the tendency of sulphur chains to oligomerise in their molten state as well and oxidation.[10] Calc. for $S_{16}C_{20}H_{24}$ (MW 777.44): C, 30.90; H, 3.11; S, 65.99. Anal. Found: C, 35.85; H, 3.55; S, 56.17. XPS analysis gave S2p [binding energy] peaks at 163.58 eV and 164.68 eV, consistent with that of elemental sulphur (see S5.5†).

Several types of nanoparticle were incorporated into the DIB cross-linker, including: Au,[11–13] InP/ZnS quantum dots,[14,15] Fe_3O_4,[16] CoO,[13,16] and PbS nanocrystals[17] (section S2 for syntheses†). All were capped with long-chain hydrocarbon ligands such as oleic acid, 1-dodecanethiol or trioctylphosphonic acid, making them readily dispersible in hydrophobic solvents and DIB. On addition to the molten sulphur, nanoparticle-DIB dispersions tended to cause effervescence, postulated to be due to the presence of excess nanoparticle surfactants in a near boiling solution, and the overall colour of the mixture changed to reflect the type of added nanoparticles.

The sulphur-polymer nanoparticle composites were analysed using a variety of techniques including: Transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS) mapping, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and UV/vis spectroscopy. Extra compositional analysis on the sulphur polymer was carried out using elemental analysis and X-Ray photoelectron spectroscopy (XPS). Solution phase characterisation was severely impaired by the insolubility of the composites in most solvents (only sparingly soluble in 1,2-dichlorobenzene).

The composites themselves exhibited the colour of the embedded nanoparticles and retained the shape of any mould in which they were placed before curing, realising the potential for complex engineering components to be cast (see Fig. 1c and d). The incorporation of nanoparticles did little to alter the physical properties of the sulphur polymer as evidenced by the melting behaviour recorded by TGA/DSC (see S5.6†), and all samples exhibited thermoset polymer characteristics. SEM micrographs supported this observation with the polymer shown to have sharp, glass-like features, with no observable difference in external structure or integrity with incorporated nanomaterials (see section S5.2†).

TEM was used to image the nanomaterials in the polymer, although this was challenging due to the insolubility of the composites for sample preparation and the high electron density of the sulphur polymer (relative to a conventional, organic polymer). This was overcome by partially dissolving the composite in 1,2-dichlorobenzene overnight, effectively giving cross-sections of the composite. TEM micrographs are shown in Fig. 2.

The PbS nanoparticles grew in size when incorporated into the composite. The diameter increased from 3.6 ± 0.5 nm in the as synthesised[17] sample to 36 ± 9 nm in the composite. The shape of the nanoparticles also changed from spherical to cubic, the latter consistent with the cubic halite structure of PbS (galena - see Fig. S5.3.4†). EDS mapping (Fig. 2f-h) clearly indicated the presence of sulphur and lead with the lead localised to the nanoparticles and the sulphur distributed throughout, indicating a full sulphur-polymer coat.

The EDS spectra of the other nanoparticle composites can be found in section S5.4† where the elemental compositions are confirmed. The most interesting sample is that containing the InP/ZnS as the quantum dots are visible by TEM. EELS mapping of sulphur and iron (Fig. 2b-d) in the Fe_3O_4-sulphur polymer composite demonstrated the presence of unaltered spherical iron oxide nanoparticles within the polymer, with the iron and sulphur glowing white in respective micrographs. TEM images of other nanoparticle-sulphur polymer composites can be found in section S5.3†.

On visible inspection, it was clear that the incorporated nanoparticles had altered the optical absorption properties of the material (Fig. 3). This was evaluated by the UV/vis absorption spectroscopy of composite thin films, with the previously stated amount of nanoparticles (∼ 0.1 g) causing an observable difference in absorption.

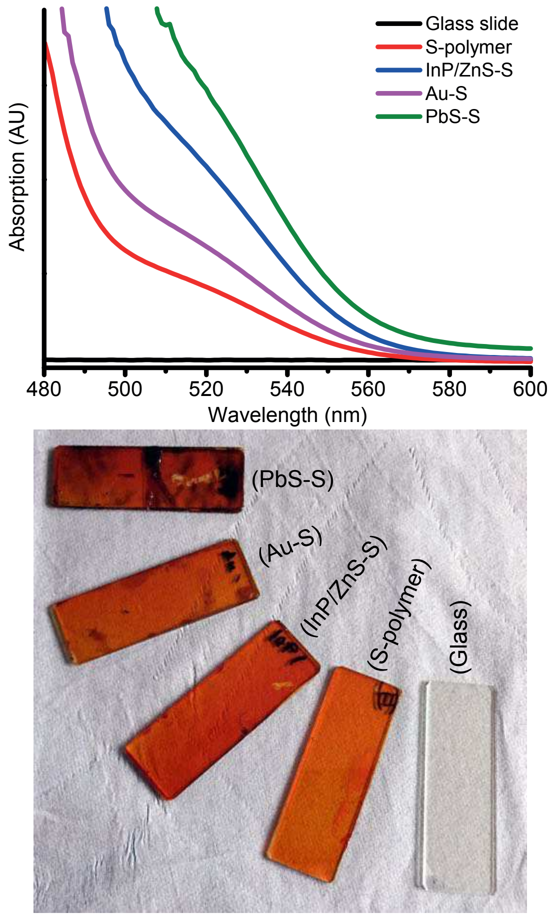

Fig. 3 Top: UV/visible spectra of various nanoparticle containing S-polymer films. Bottom: Image of films produced.

The band-edge of the PbS parent nanocrystals was not observable in the PbS-sulphur polymer composite, presumably due to temperature induced agglomeration destroying the quantum dot properties. Absorption spectra of PbS nanocrystals and composite in the infrared range are given in Figure S5.7.3†. The gold nanoparticle-sulphur polymer composite does show the surface plasmon resonance band of the gold, albeit blue-shifted compared to the parent material dispersed in toluene (Figure S5.7.1†). This is again consistent with ripening as confirmed by TEM images, with a size increase from 4.7 nm ± 1.2 nm to 22.3 nm ±19.2 nm, although smaller particles of near original size do remain (Figure S5.3.2†).[18] The band-edge of the InP/ZnS quantum dots (455 nm in *n*-hexane) used was not detectable in the UV/vis spectrum due to high absorption of light by the sulphur polymer matrix in that region, however they were visible by TEM microscopy.

For the first time, sulphur inverse vulcanisation polymers have been used as a matrix for inorganic nanoparticles with tuneable optical properties. Composites were synthesised by mixing pre-formed, hydrophobically ligated nanoparticles, including Au, InP/ZnS quantum dots, Fe_3O_4, CoO, and PbS nanocrystals, with the DIB cross linker, creating an homogeneous dispersion. The composites are easily mouldable into any shape, and have tuneable physical and mechanical properties depending on the amount of DIB used. The versatility of these materials coupled with the "waste" nature of sulphur, potentially make these a viable alternative to hydrocarbon-based polymer composites, for the synthesis of a new generation of smart-materials.

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